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PHASE I REPORT

APPLICABILITY OF ORGANIC SOLIDS TO THE DEVELOPMENT OF NEW TECHNIQUES FOR REMOVING OXIDES OF SULFUR FROM FLUE GASES

10669-6003-R0-00

31 OCTOBER, 1968

PREPARED FOR:

NATIONAL CENTER FOR AIR POLLUTION CONTROL
UNDER CONTRACT NO. PH22-68-46

TRW
SYSTEMS GROUP
ONE SPACE PARK
REDONDO BEACH, CALIFORNIA

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By

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Prepared for:

National Center for Air Pollution Control
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31 October 1968

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1.0 INTRODUCTION AND SUMMARY

This Phase I comprehensive report describes the work performed by TRW Systems Group for the National Center for Air Pollution Control under Contract No. Ph-22-68-46 during the period of 24 June through 30 September 1968. This work had the following objectives:

- To perform a detailed library search and selection of most promising organic solids for removing sulfur dioxide from flue gas, and
- To perform a preliminary chemical systems analysis for candidate SO_2 removal materials.

As a result of a detailed literature search and conceptual analysis, a number of organic solids were identified as having capacity for the binding of sulfur dioxide. A principal accomplishment of this task was the identification of a number of waste materials which have high potential for removal of SO_2 from flue gases. Organic materials were selected on the basis of:

- Known ability to take up sulfur dioxide,
- Price and availability,
- Thermal stability,
- Regenerability, and
- Mechanical properties.

Five organic materials were identified which offered promise for removing sulfur dioxide from flue gases:

- Cellulosics,
- Nigrosin,
- Poly(N-vinylcarbazole),
- Pyrolyzed poly(vinylchloride), and
- Pyrolyzed poly(acrylonitrile).

The specific cellulosics selected are: waste newsprint, sawdust and cotton. Although a number of other inexpensive cellulosic based materials ought to be evaluated the limitations of Phase II required that the scope be narrowed.

The results of the preliminary chemical systems analysis demonstrate that organic solid sulfur dioxide recovery from flue gases is, in general, economically feasible where certain criteria are met. The preliminary chemical systems analysis was keyed to thermal regeneration of the organic solids, however, in the case of cellulosic materials chemical reaction and conversion of the products to useful commodities may also be a feasible process. However, as so little is known as to the parameters involved in these conversion processes at the present time, a consideration of this type of regeneration was not included in the preliminary chemical systems analysis.

2.0 LITERATURE SEARCH

ORGANIC SOLIDS FOR SULFUR DIOXIDE REMOVAL FROM FLUE GASES

A comprehensive literature search through Chemical Abstracts subject heading for sulfur dioxide was completed from the year 1907 to the present. All pertinent sub-categories of the heading sulfur dioxide were search in detail, e.g., reaction of, reaction with, absorption, etc., with special reference to reaction with organic solids. Thirty-three references were found which dealt with the interaction of sulfur dioxide or nitrogen oxides with organic solids. Of these, only those concerned with the use of ion exchange resins addressed themselves to the specific problem of removing sulfur dioxide from gas mixtures and none of the ion exchange papers discussed the temperature region applicable to flue gas stacks (these being 215-300°F after the preheater region of the flue gas stack and approximately 600-650°F before the preheater region). This lack of high temperature testing of the ion-exchange resins is probably due to the fact that most of the resins contain either pendent amino groups or single-strand organic backbones which are relatively thermally unstable. Several references provided information showing that cellulosic materials take up appreciable quantities of SO_2 at room temperature. It had originally been hoped that data such as adsorption and desorption rates of sulfur dioxide, activation energies of organic solid-gas reactions, etc., at room temperature, or better flue gas stack temperatures, would be available from the literature. Unfortunately, where references were found to be specific for organic solid-sulfur dioxide interactions, these studies were conducted almost entirely at temperatures equal to or well below room temperature.

The results of the literature search and conceptual studies are presented below in three sections:

- Organic solids which interact with sulfur dioxide,
- Criteria for selection of most promising organic solids, and
- Most promising organic solids for removal of sulfur dioxide from flue gases.

2.1 ORGANIC SOLIDS WHICH INTERACT WITH SULFUR DIOXIDE

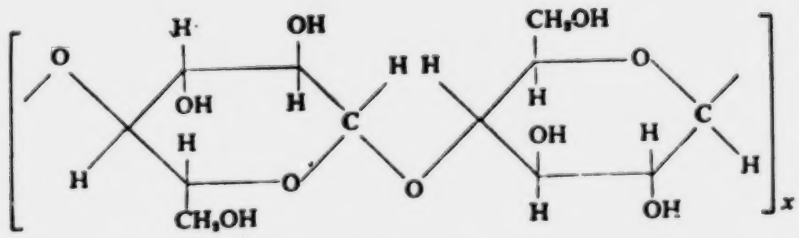
Approximately 32 references were found which described the interaction of sulfur dioxide with organic solids. The information contained in these references is summarized in Table I which contains a classification of organic solid-SO_2 interactions, together with information generated at TRW Systems prior to the start of this contract. In this section, each organic solid will be discussed individually in the following organic solid subdivisions:

- Polymers - cellulosics,
- Polymers - ion exchange,
- Polymers - miscellaneous,
- Homocyclic aromatics and derivatives,
- Heterocyclic aromatics and derivatives,
- Telomeric dyes and dye bases, and
- Organo-metallics

2.1.1 Polymers - Cellulosics

Cellulose is obtained from and makes up a large part of the structure of wood, cotton, ceral, straw, hemp and jute among others. Paper is a major commercial cellulosic product which consists largely of cellulose that also includes fillers, binders, and pigments. The 1966 total U. S. production of paper products was 46.5 million tons which included the following major forms: paper, paperboard and construction paper, while the total newsprint consumption in the U.S. was 9.1 million tons of which 6.7 million tons were imported from Canada.

Cellulose is a ladder polymer



Cellulose

TABLE I

CLASSIFICATION OF ORGANIC SOLID - SO_2 INTERACTIONS

Organic Solid Type	Organic Solid	Interactions	References
Polymer	Cellulosics (paper, wood cotton), etc.	Insertion, change-transfer	2 - 8
	Ion exchange resins (divinylbenzene-methylvinylpyridine copolymer and other amine containing polymers)	Change-transfer, acid-base	9 - 15
	Poly(N-vinylcarbazole)	Change-transfer, acid-base	21
	Pyrolyzed Poly(acrylonitrile)	Change-transfer, acid-base	21
	Conjugated double bond containing resins pyrolyzed poly(vinyl-chloride)	Addition	22
	Linear saturated polymers (Teflon, poly(propylene), poly(vinyl-chloride, etc.)	Absorption-Adsorption	16 - 20
Homocyclic Aromatics and Derivatives	Anthracene	Change-transfer	23 - 24
	Hydroquinone	Inclusion compound	25 - 26
	Coal*	Change-transfer, acid-base	27
Heterocyclic Aromatics and Derivatives	Phenothiazine	Change-transfer, acid-base	28
	Dianin	Inclusion compound	29 - 30
Hydrocarbons and Derivatives	Camphor	Change-transfer	31
	Cyclohexylhydroxylamine	Insertion	32
Telomeric Dyes and Dye Bases	Nigrosin	Change-transfer, acid-base	21
	Copper Phthalocyanine	Change-transfer, acid-base	22
Organo Metallics	Tri-n-dodecyl aluminum	Insertion	34
	Alkali metal salts of fatty acids Alkali metal salts of benzoic acid	Insertion, acid-base	33

*Coal is a complex mixture of homocyclic and heterocyclic aromatics.

which because of this is highly thermally stable. Cellulose materials generally do not begin rapid thermal decomposition below 500-600°F (1). Hence, cellulose derivatives from a thermal stability standpoint are applicable to flue gas stack region in the area after and possibly before the preheater. Take up of sulfur dioxide and other gases by cellulose has been studied in some detail at or near room temperature. It has been shown that cellulose itself absorbs, in order of decreasing volume: sulfur dioxide, carbon dioxide and oxygen (this is the same order as charcoal) (2). It has also been shown that sulfur dioxide absorption by various cellulose derivatives varies according to the heat pretreatment of the cellulose derivative (3). At room temperature, hydrophilic cotton absorbs 3% by weight sulfur dioxide, filter paper, 3.2% by weight, filter paper heated at 173°C prior to sorption 4.3%, filter paper heated to 320°C takes up 2.98%, hydrophilic cotton heat dried at 150°C takes up 13.88% and nitro cellulose takes up 16.89%. In another paper it is stated that wood takes up more sulfur dioxide than does cotton (4), and that carbon dioxide is not appreciably absorbed by wood. Galzova shows that sulfur dioxide is taken up by cotton during a drying process (5), while Hudson shows that printing paper takes up very small amounts of sulfur dioxide from the atmosphere under ambient conditions (6 - 8).

It is clear from these results that sulfur dioxide is taken up in appreciable quantities, as much as 17% by weight at room temperature by cellulosic materials. This uptake probably occurs by a combination of charge-transfer interactions and insertion reactions.

CHARGE TRANSFER

$$\text{CELLULOSE} + n\,SO_2 \rightleftharpoons \text{CELLULOSE}\cdot(SO_2)_n$$

$$K_{equil} = \frac{[\text{CELLULOSE}\cdot(SO_2)_n]^n}{[\text{CELLULOSE}]\,[SO_2]^n} \qquad (1)$$

CHEMICAL REACTION

$$\text{CELLULOSE}\text{-}(OH)_n + nSO_2 \rightleftharpoons \text{CELLULOSE}\text{-}(OSO_2H)_n$$

$$K_{equil} = \frac{[\text{CELLULOSE}\text{-}(OSO_2H)_n]^n}{[\text{CELLULOSE}\text{-}(OH)_n]\,[SO_2]^n} \qquad (2)$$

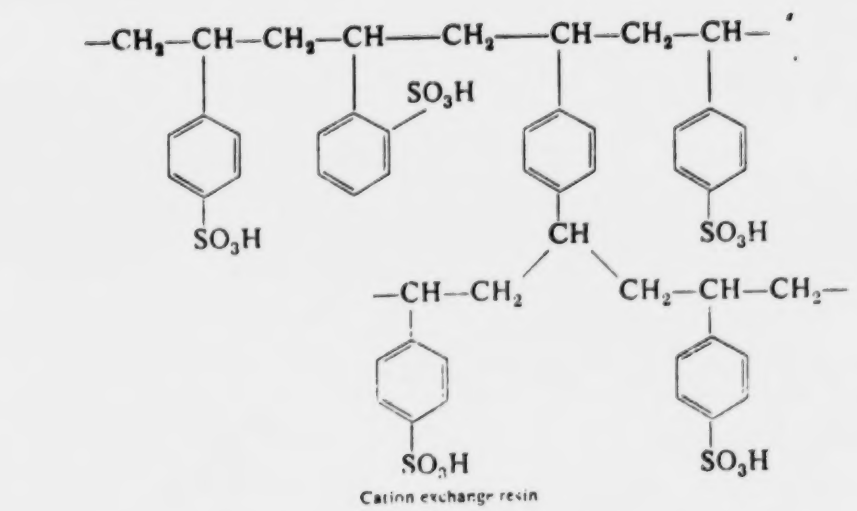
Change transfer interactions (Equation 1) are generally exothermic processes and the equilibrium constants decreases as temperature increases, as does ordinary sorption. Thus the higher temperatures encountered in flue gases will tend to decrease strongly this type of sulfur dioxide uptake. However, it is hoped that the major part of the SO_2 uptake is due to the second reaction, that of insertion (Equation 2). This is a chemical reaction which will very likely be endothermic and higher temperatures will increase the equilibrium constant rather than decrease it. Thus, it may be anticipated that sulfur dioxide uptakes of from 5 to 10% may be found for at least some of the cellulosic containing materials at flue gas temperatures of 215-300°F. Indeed, a rough feasibility test utilizing a gas stream which was 30% SO_2 w/w in nitrogen showed an uptake of SO_2 at 215°F by ground waste newsprint. There are a number of "regeneration" possibilities for cellulose materials:

- Regeneration of cellulose and sulfur dioxide by use of heat, inert gas, vacuum, solvent extraction (water, amines, etc.)
- Hydrolysis of cellulose to glucose by action of bound sulfur dioxide (from flue gas) together with water.

It is very difficult to set absolute prices for these materials as the prices are highly variable depending on the quality and grade. It has, however, been ascertained that waste paper can be obtained for roughly 0.3 cents per pound. This compares quite favorably with the price of activated charcoal of 10 cents per pound. Of course, it is readily apparent that all of the cellulosic materials are extremely inexpensive relative to pure chemical compounds or activated charcoal. This brief study, which will survey a number of other organic solid classes, must limit itself to a few cellulosics, specifically: sawdust, (approximately 50% cellulose), cotton, (almost 100% cellulose), and waste paper specifically newsprint (roughly 75% cellulose).

2.1.2 Polymers - Ion Exchange

Ion exchange resins both cation and anion types have been studied in some detail with regard to their ability to sorb sulfur dioxide. The structure of typical cation and anion exchange resins are shown in the figure below.



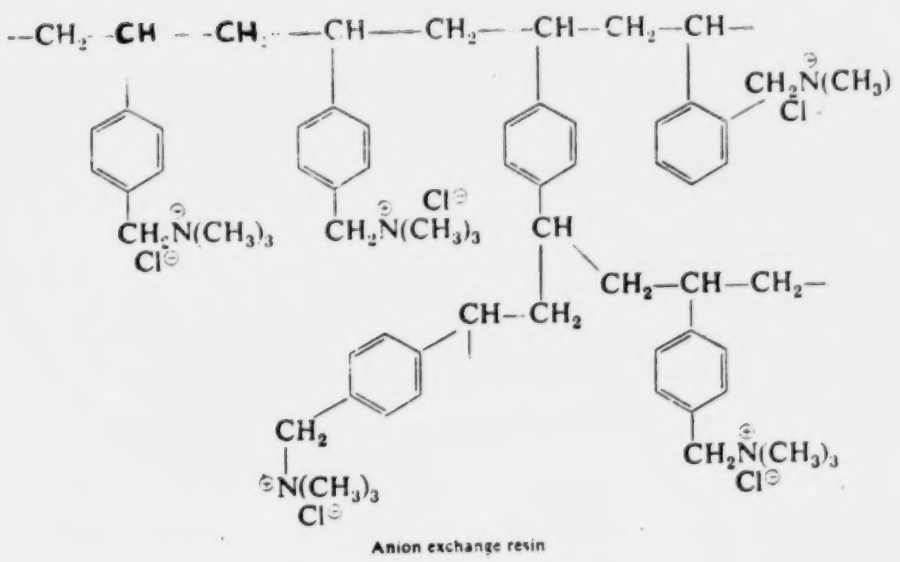


Figure 1. Structure of Ion Exchange Resins

As much as 0.25 gram of sulfur dioxide per gram of ion exchange resin has been reported to be obtained at room temperature for typical ion exchange resins

at equilibrium (9) and comparisons have been made between ion-exchange resins and typical inorganic sorbents such as activated charcoal, molecular sieve and silica gel (9-13) in which the ion exchange resins were shown to be satisfactory for low temperature sorption but not equivalent to the inorganics. Clearly, the linear structure of ion exchange resins coupled with the thermal instability of the pendent acid and base groups limits their use in actual flue gas environments. It has been shown that ion-exchange resins based on copolymers of 2-methyl-5-vinylpyridine and p-divinylbenzene sorb sulfur dioxide from moving gas streams at low temperatures (60°C), and these sorbents may be regenerated by combination of hot air and ammonia, or sulfur dioxide may be oxidized to sulfur trioxide on the catalytic surface formed by the ion exchange resin, again at relatively low temperatures (14, 15).

2.1.3 Polymers - Miscellaneous

Several researchers have studied the interactions of sulfur dioxide with various construction materials including plastics at ambient levels (1 to 100 pphm. vol.) and at ambient temperatures (20-35°C) (16-19). These workers have shown that materials, such as stainless steel, Teflon, Tygon, glass, poly(propylene), poly(vinylchloride), etc., sorb small amounts of sulfur dioxide from the atmosphere. Further, it has been shown that sulfur dioxide, nitrogen oxide, etc., catalyze thermal decomposition of poly-(tetrafluoroethylene) at 450-500°C (20). However, the nature of these materials and the low degree of sulfur dioxide sorption coupled with relative thermal instability indicates that they are of little interest with regard to the problem of removing sulfur dioxide from flue gases.

Recent studies at TRW Systems have shown that TRW processable polyimides ($10-30/lb for prepolymer), poly(N-vinylcarbazole) ($5/lb), and 8-hydroxyquinoline-formaldehyde polymer (unavailable commercially) remove sulfur dioxide from moving gas streams at 460°F (on fire brick) (21), and these organic solids are thermally stable according to thermogravimetric analysis in air at temperatures encountered in flue gas stacks. However, the high price of the polyimide and relative unavailability of the formaldehyde polymer limit their potential. The change-transfer interaction of N-vinylcarbazole with SO_2 is shown in Figure 2.

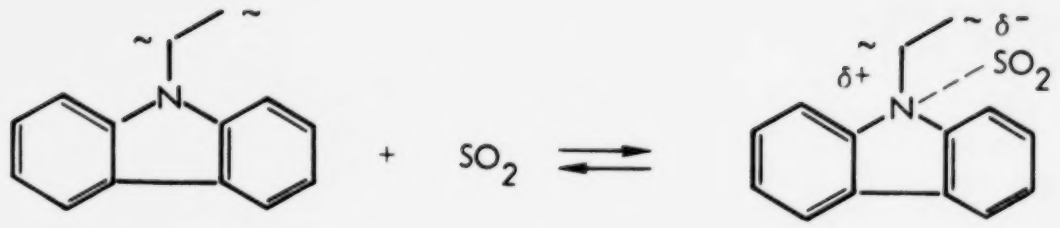


Figure 2. Change-Transfer/Acid-Base Interaction of N-vinylcarbazole with SO_2

In addition, subsequent experimental evaluation at TRW Systems has shown that pyrolyzed poly(acrylonitrile) ($0.60/lb for polyacrylonitrile) and pyrolyzed poly(vinylchloride) ($0.15/lb for poly(vinylchloride), however, as a possible waste product it could cost only the price of transportion), also takes up sulfur dioxide from moving gas streams (22) probably via change-transfer or acid-base (Figure 3) and addition reactions Figure 4) respectively.

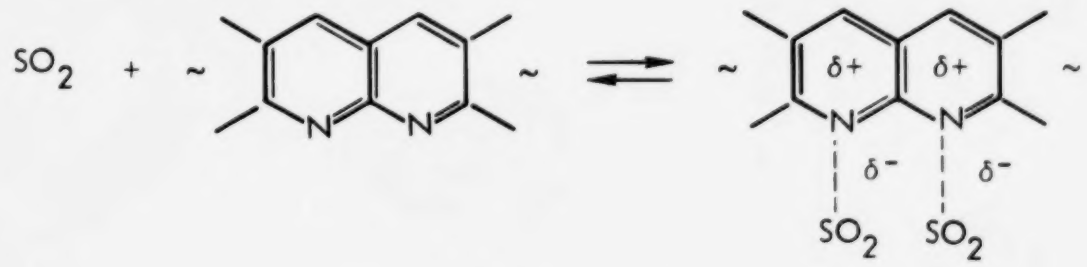


Figure 3. Change-Transfer/Acid-Base Interaction of Pyrolyzed Poly(acrylonitrile) with SO_2

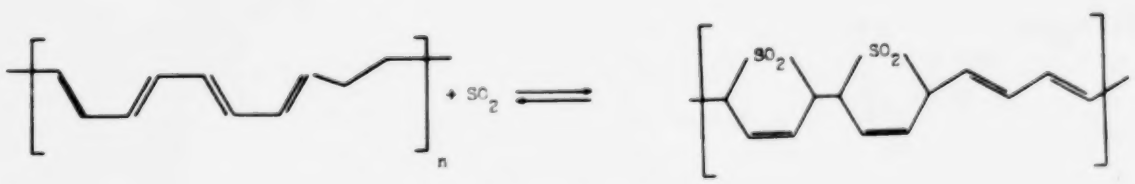


Figure 4. Addition Reaction of Pyrolyzed Poly(vinylchloride) with SO_2

2.1.4 Homocyclic Aromatics and Derivatives

Anthracene has been shown to sorb sulfur dioxide, nitrogen dioxide and oxygen all of which produce a marked increase in the surface photoconductivity of anthracene crystals (23, 24). Hydroquinone takes up (by inclusion compound formation) sulfur dioxide, nitrogen oxide, carbon monoxide and carbon dioxide gases at room temperature and reverts to hydroquinone and gas at approximately 250°F (25, 26), and coal, a complex combination of homocyclic and heterocyclic aromatics has been shown to take up sulfur dioxide at about 300°C with conversion of some of the sulfur dioxide and chemical alteration of the coal (27).

2.1.5 Heterocyclic Aromatics and Derivatives

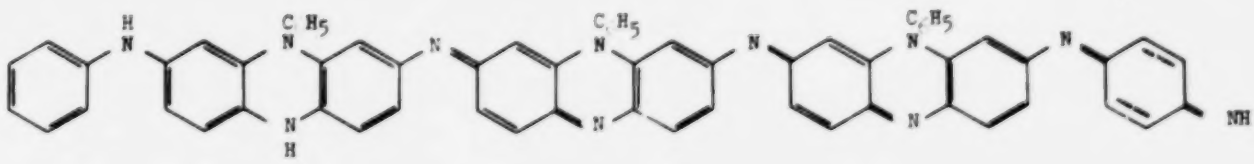
Phenothiazine forms an equimolar complex with sulfur dioxide in solution which is regenerable in the solid state by evaporation of sulfur dioxide at room temperature under vacuum (28). Dianin,(p-3,4-dihydro-2,2,4-trimethyl-2-H-1-benzopyran-4-yl) phenol, forms inclusion compounds with sulfur dioxide and other flue gas components. The molecular structure of these inclusion compounds or clathrates have been studied in detail by infrared spectroscopy (29, 30).

2.1.6 Hydrocarbons and Derivatives

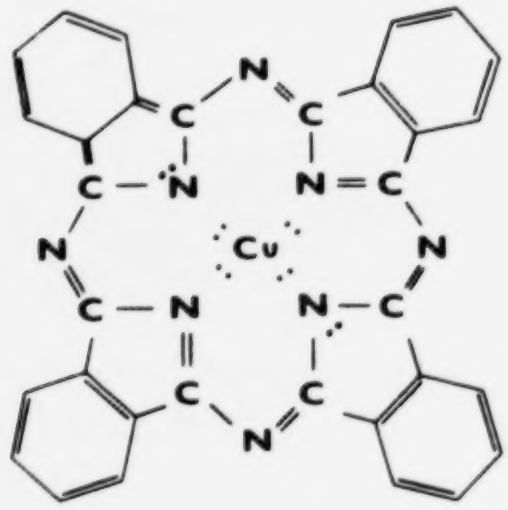
Camphor forms 1:1 and 1:2 complexes with sulfur dioxide above -16°C. Equilibrium pressures of the camphor-sulfur dioxide system were measured at several temperatures ranging from -38° to +38°C (31). Cyclohexylhydroxylamine reacts with sulfur dioxide at -10°C to give cyclohexylsulfamic acid (32).

2.1.7 Telomeric Dyes and Dye Bases

Recent studies at TRW Systems have shown that nigrosin ($2.75/lb), an aniline black derivative (21),



and copper phthalocyanine (22),



remove sulfur dioxide from moving gas streams at 460°F. No mention of either of these dyes or indeed of any dyes was found in the literature with regard to take up of sulfur dioxide. It appears that these dyes, which are highly thermally stable, take up sulfur dioxide by charge-transfer or possibly acid-base interactions.

2.1.8 Organo Metallics

Alkali metal salts of benzoic and fatty acids add gaseous sulfur dioxide at a slow rate in the ratio of approximately 1 mole of sulfur dioxide to 1 mole of compound at temperatures above 0°C (33). Tri-n-dodecyl aluminum reacts with 3 moles of sulfur dioxide per mole of compound yielding aluminum trisulfonates which can later be hydrolyzed to sulfamic acids (34).

2.2 CRITERIA FOR SELECTION OF MOST PROMISING ORGANIC SOLIDS

At this point in the program, the basic criteria which may be used for the selection of organic solids for Phase II evaluation for the removal of sulfur dioxide from flue gas emission stacks, are the following:

- Ability of sorbent to remove SO_2 from flue gas at operating temperatures at a high rate,
- Thermal stability of sorbent,
- Cost and availability of sorbent, and
- Mechanical properties.

It is clear that the primary requirement of the organic solid for the removal of sulfur dioxide from flue gases is ability to remove sulfur dioxide selectively from moving gas mixtures at the flue gas operating temperatures and at a relatively high rate (typical contact times are in the order of a second). The sorbent must be thermally stable at the temperature of sulfur dioxide uptake (215°F minimum after the preheater region) for at least several minutes. If the sorbent is to be regenerated thermally, it must be stable at even higher temperatures (approximately 600°F) for a period of minutes. The organic solid must be capable of being regenerated or converted to useful products. Regenerability modes could include heat, inert gas, vacuum, solvent extraction, catalytic oxidation, or conversion of the reaction product to a useful commodity chemical. The availability of inexpensive organic solids in large quantities and without any laborious modifications is of major importance. Finally, the mechanical properties of organic solid must be such that the solid is amenable to use in a sorption configuration. That is, the organic solid must be either reasonably porous and finely divided itself or capable of being coated onto a high surface area substrate such as fire brick or activated charcoal.

2.3 MOST PROMISING ORGANIC SOLIDS FOR REMOVAL OF SULFUR DIOXIDE FROM FLUE GASES

Seven specific organic solids were selected for Phase II experimental evaluation on the basis of the criteria stated in Section 2.2. These organic solids are:

- Newsprint (paper),
- Sawdust,
- Cotton,
- Nigrosin,
- Pyrolyzed poly(acryonitrile),
- Pyrolyzed poly(vinylchloride), and
- Poly(N-vinylcarbazole).

The properties of these organic solids as related to the criteria for sulfur dioxide removal are presented in Table II. The organic solids which were selected are all known to take up sulfur dioxide, be thermally stable at flue gas temperatures, to be low in cost, have good mechanical properties and have potential for regenerability. Monomeric organic solids even though known to take up sulfur dioxide were eliminated from this study (e.g., anthracene, phenothiazine, etc.) because of their lack of mechanical properties, that is, they cannot be coated on inert substrates nor can they form mechanically sound sorbent particles. The ion exchange resins were eliminated from this study as they are being evaluated on other NCAPC programs. Polyimides and 8-hydroxyquinoline-formaldehyde polymers were discarded from further consideration because of their very high price.

TABLE II

PROPERTIES OF MOST PROMISING ORGANIC SOLIDS FOR SO_2 REMOVAL

Organic Solid	SO_2 Uptake	Thermal Stability: Before Pre-heater 550-650°F (Reg. 2) After Pre-heater 215-300°F (Reg. 1)	Regenerability	Cost and Availability	Mechanical Properties
1. Newsprint (paper 2. Sawdust 3. Cotton	Known to take up SO_2 at R.T. and preliminary results show take up at 215°F by paper	Basic constituent (cellulose) stable region 1	Heat, wash or chemical conversion possible	Waste materials cost of transportation	Can be used as is, ground or shredded, etc.
4. Nigrosin	Known to take up SO_2 at 460°F	Stable regions 1 and 2	Heat or wash possible	$2.75/lb. in ton quantity	Can be coated
5. Pyrolyzed Poly (acrylonitrile)	Known to take up SO_2 at 460°F	Stable regions 1 and 2	Heat or wash possible	Poly(acrylonitrile) $0.68/lb in any quantity	Can be coated
6. Pyrolyzed Poly (vinylchloride)	Known to take up SO_2 at 460°F	Stable region 1	Heat or wash possible	Poly(vinylchloride), waste material, cost of transportation	Can be coated
7. Poly(N-vinylcarbazole	Known to take up SO_2 at 460°F	Stable region 1	Heat or wash possible	$5.00/lb in ton quantity	Can be coated

3.0 PRELIMINARY CHEMICAL SYSTEMS ANALYSIS

This section presents the results of a preliminary chemical systems of processes using organic solids to control sulfur dioxide emissions from flue gases. It was the objective of the analysis to develop preliminary process designs capable of estimating the capital investment and operating costs of systems employing organic solid sorbents and thereby demonstrate the feasibility of these processes.

A large part of the SO_2 pollution problem, 46% of the total in 1966, can be attributed to SO_2 emission from electricity generating power stations. Of the emissions from power stations in 1966, about 91% came from the combustion of coal and about 9% from oil (35). In view of these factors, the preliminary analysis was directed toward the development of a process which could be incorporated into a coal burning power plant. A consideration of the capital expenditure involved in a process capable of handling the large inventory of organic solid sorbent required to control the SO_2 emission from an "average" power plant led to the choice of a fixed-bed mode of operation. A mathematical model, applicable to polymeric organic solid sorbents as well as monomeric sorbents, was formulated to simulate a fixed-bed sorption column, and the model was then translated into a FORTRAN II computer program.

In Section 2.3, candidate organic solids for removal of sulfur dioxide from flue gases were assessed in terms of system criteria and as a result seven organic solids were selected for Phase II evaluation. Of these, the cellulosics appeared to most clearly satisfy the criteria. For example, the 46.5 million tons of paper products produced in the U.S. in 1966 is in line with the estimated 28 million tons of SO_2 per year (approximately 13 million tons of SO_2 per year can be attributed to power station stack gases) emitted to the atmosphere in the U.S. (35). The price of waste paper, roughly 0.3 cents per pound, compares favorably with the price of other sorbent materials(waste paper is approximately 1/30th the price of activated charcoal). In addition, cellulose does not begin rapid thermal decomposition below 500-600°F and, hence, could be used in the gas stack region after the air preheater. Finally, the ability of cellulose to sorb significant amounts of sulfur dioxide has been reported in the literature.

A process, based on a regenerative fixed-bed SO_2 sorption system with sulfur recovery capability, was specifically designed for a cellulose (paper) sorbent. A computer program, written to evaluate the capital and operating costs of the proposed cellulose - SO_2 sorption process, was combined with the fixed-bed computer program and then utilized to determine the cost sensitivities of the selected independent parameters. The computer program output, which included operating and capital costs, as well as process condition information (sorption batch time, amount of SO_2 sorbed on paper, etc.), is presented in graphical form and can be used to identify operating regions which will result in the maximum profit. The graphs are also an aid in evaluating the effect of a process parameter on the process operating cost.

The results of the preliminary analysis indicates that the proposed cellulose - SO_2 recovery process is economically feasible. In particular, the computer simulation of the proposed process, operating at the selected base case conditions, calculated that a profit of $941,000 would be netted per year (42 cents/ton coal). The total capital requirement would be $2,770,000.

A further consequence of the preliminary chemical system analysis was the development of a computer capability, applicable to a wide range of problems involving SO_2 removal and recovery, which can be adapted to any solid sorbent material operated in batch manner. Only minor revisions in the proposed SO_2 recovery system would be required if organic solids (e.g., nigrosin, pyrolyzed polyacrylonitrile, pyrolyzed polyvinylchloride) were to replace paper as the SO_2 sorbent. Some indication of the effect of sorbent cost on the process operating profit for a SO_2 recovery system equivalent to the proposed system but using a general sorbent material is included in this report.

The results of this study are described under the following five categories below:

- Process Description
- Process Model
- Process Base Conditions
- Results of Parametric Analysis
- Conclusions

The computer program is presented in the Appendix (Section 4.0).

3.1 PROCESS DESCRIPTION

A process for removing and recovering SO_2 from flue gas streams has been developed utilizing the SO_2 sorption capability of cellulose (paper). Figure 5 is the flowsheet of the proposed process as it might be incorporated into a coal-burning power plant (or with minor changes to an oil-burning power plant). There are wide variations between power plants with regard to boiler configuration, the arrangement of heat-recovery equipment, and the temperatures at various positions in the plant, and therefore, the optimum configuration could vary from the one selected here to illustrate the general characteristics of the proposed SO_2 recovery system in a power plant. Although the following process description will apply directly to the paper - SO_2 recovery system of Figure 5, only slight modifications would be required if another organic solid sorbent is used. The major equipment items in the recovery system are three carbon steel sorption columns, a paper shredder, and an induced draft fan. It is believed that three columns may be necessary to assure adequate time to regenerate and replace the paper between each sorption run. Because of the large quantity of sorbent material which must be handled to control the SO_2 emission from a power plant, it was determined that the lowest capital expenditure would result from a fixed-bed mode of operation. If the amount of required sorbent could be significantly reduced below current estimates, a system using fluidized beds or rotating disc contactors may prove economically advantageous. The location of the induced draft fan will be dependent on operating conditions of a particular system and, for this reason, is shown in two possible positions in Figure 5.

The operation of the SO_2 recovery system, as illustred in Figure 5, consists of three phases:

- Sorption of SO_2 by the paper.
- Regeneration of the paper and recovery of the SO_2.
- Replacement of the spent paper.

The high SO_2 content flue gas, after passing through the power plant's dust collector and spark eliminator, enters the fixed-bed sorption column, packed with shredded paper. The SO_2 in the flue gas is sorbed on the paper,

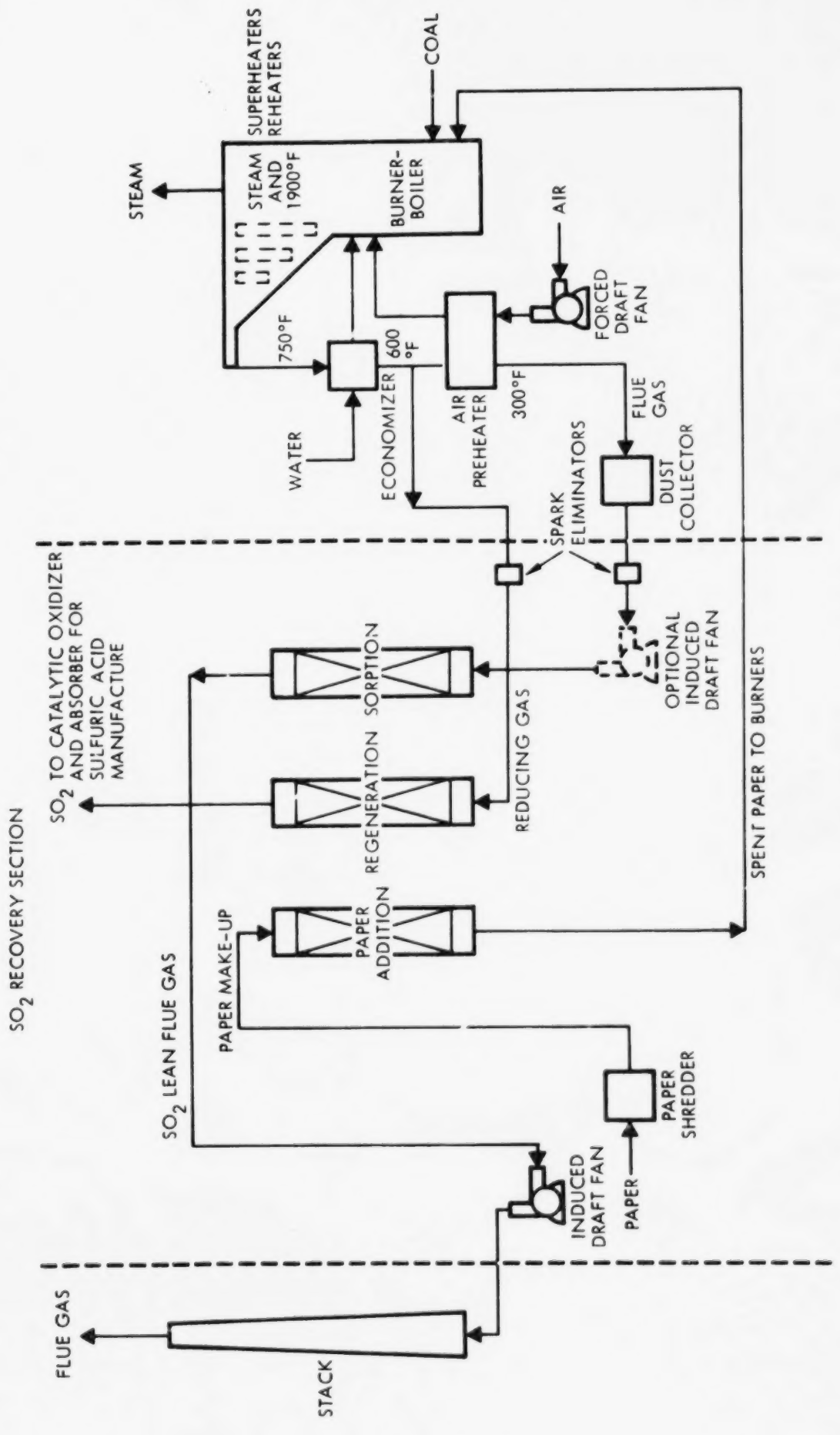


Figure 5. Coal Burning Power Plant with SO_2 Recovery Capability

and the flue gas, after exiting from the column, is sent to the power plant's stack. The paper also entrains any fly ash that passes through the dust collector. The column operates in this mode until the SO_2 content of the flue gas exiting from this column exceeds the specified pollution limits. When the paper no longer sorbs an adequate amount of SO_2, the flue gas stream is fed to one of the other columns.

After completion of the sorption mode, the paper in the column undergoes regeneration by passing hot flue gas (600°F) through the column, causing the SO_2 on the paper to desorb. The hot flue gas is drawn from the line separating the economizer (water preheater) and the air preheater. The SO_2 rich gas leaving the column during the regeneration mode is sent to a catalytic oxidizer and converted to SO_3. The SO_3 then undergoes further processing to sulfuric acid.

After regeneration of the paper is completed, some of the paper at the bottom of the column is withdrawn and sent to the burners as fuel. Fresh paper makeup is conveyed from the shredder and added at the top of the column. The column is then ready to begin the sorption mode again.

Stability problems during upsets in the flue gas generating device were not apparent in the proposed process. For example, a temperature runaway in the power plant's boiler would be partially damped in the economizer and air preheater. The flue gas must also pass through spark eliminators which have the capability of spraying water into the gas stream. Even if a fire did occur in a column, the flue gas stream could be diverted to the stack and the fire quickly quenched by a water spray system in the column.

Another problem which could arise is a boiler tube rupture which would send a large amount of steam and water into the system. The water and steam should not cause any serious deterioration of the paper. Along a similar line, an oxygen deficiency in the boiler or a failure of the dust collector, resulting in large amounts of carbon entering the SO_2 recovery system, should not adversely affect the paper and, in fact, the paper would entrain the solid particles in the flue gas.

No major stability problems relating to the SO_2 recovery system itself were uncovered. Paper transfer within the columns will take place

by internal vibration. If complete blockage of the paper should occur, manual replacement of the paper would be possible until the problem is rectified. A water spray system will be built into the system as a precaution against fires, and even if a fire does occur in a column, it should not cause extensive damage to the equipment.

Since the spent paper is used as fuel in the boiler, the sorbent does not cause secondary pollution problems. The only secondary pollution should be that encountered in a modern sulfuric acid plant provided the recovered SO_2 is converted to sulfuric acid.

3.2 PROCESS MODEL

3.2.1 Derivation of Mathematical Model

A mathematical model containing technical and economic variables of interest was formulated for the proposed SO_2 recovery process. Since the sorption columns are the major cost items in the process, the technical portion of the model was developed to simulate the unsteady-state operation of a packed bed. The economic portion of the model, utilizing information provided by the technical study, estimates the capital and operating costs of the proposed SO_2 recovery process.

The technical section of the model has the capability of determining the composition of the sorbable component in both the solid and fluid phases as a function of time and position in the column. The description of the technical model deals specifically with an SO_2-paper sorption column, but the approach is of a general form and would apply to the unsteady-state operation of any fluid-solid fixed bed column.

Consider a sorption column in which SO_2 is transferred from the gas phase to the solid phase (in this case paper). With reference to Figure 6, let

G = superficial flue gas flow rate, $\left(\frac{ft^3}{hr - ft^2 \text{ empty column cross section}}\right)$

C_o = SO_2 concentration in feed flue gas (moles SO_2/ft^3)

C_G = SO_2 concentration in flue gas at position Z in the column and at time t, (moles SO_2/ft^3)

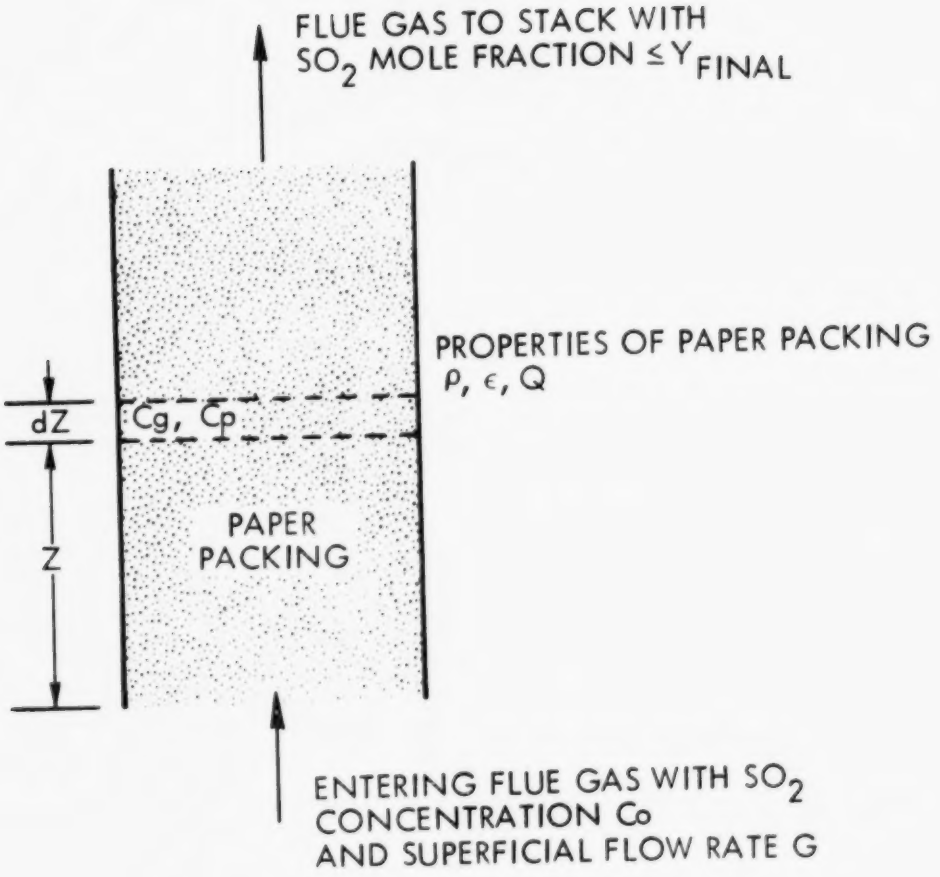


Figure 6. Unsteady-State Operation of a Packed Bed

C_P = SO_2 concentration in the paper at position Z in the column and at time t, (moles SO_2/lb paper).

Q = saturated SO_2 concentration of paper, (moles SO_2/lb paper.

Y = residual SO_2 mole ratio of the flue gas, C_G/C_o.

X = residual SO_2 mole ratio of paper, C_P/Q.

ρ = density of paper, (lbs paper/ft^3 column).

ϵ = void fraction of column (ft^3 actual volume/ft^3 empty column).

t = time, hr.

Z = column height, ft.

k_g = mass transfer coefficient, moles/(hr)(ft^2 transfer area) (moles/ft^3).

a = area for mass transfer per unit volume, (ft^2 transfer area/ft^3 column).

C_i = SO_2 concentration at fluid-solid interface, (moles SO_2/ft^3).

H = equilibrium constant, $C_i = HC_P$.

It will be assumed that C_O, Q, ρ, ϵ, k_g, a, and H are constant, that plug flow exists within the column, and that axial diffusion of SO_2 is negligible. Composition gradients within the paper will be neglected, and mass transferred by diffusion as the result of solid-solid contact will be ignored.

A material balance on the SO_2 contained in an element of unit cross section and of height dZ is

Rate of input: $GC_G = GC_oY$

Rate of output: $G(C_G + \frac{\partial C_G}{\partial Z} dZ) = GC_o(Y + \frac{\partial Y}{\partial Z} dZ)$

Rate of accumulation: $\frac{\partial}{\partial t}[\epsilon C_G + \rho C_p] dZ = \frac{\partial}{\partial t}[\epsilon C_oY + \rho QX] dZ$

The SO_2 material balance is then

$$- GC_o \frac{\partial Y}{\partial Z} = \epsilon C_o \frac{\partial Y}{\partial t} + \rho Q \frac{\partial X}{\partial t} \qquad (1)$$

or

$$\frac{\partial Y}{\partial Z} + \frac{\epsilon}{G} \frac{\partial Y}{\partial t} + \frac{\rho Q}{GC_o} \frac{\partial X}{\partial t} = 0 \qquad (2)$$

The term

$-GC_o \frac{\partial Y}{\partial Z}$ accounts for the concentration change of SO_2 caused by flue gas flow

$\epsilon C_o \frac{\partial Y}{\partial t}$ accounts for the SO_2 concentration change in the gas hold-up in the voids

$\rho Q \frac{\partial X}{\partial t}$ accounts for the concentration change of the SO_2 sorbed on the paper

Each term has units of moles/hr-ft^2 empty column cross section.

Similarly, a material balance on the SO_2 in the solid phase is

Rate of input: $k_g a (C_G - C_i) dZ$

Rate of output: 0

Rate of accumulation: $\frac{\partial}{\partial t} (\rho C_p) dZ$

the material balance is then

$$k_g a (C_G - C_i) = \rho \frac{\partial C_p}{\partial t} \qquad (3)$$

This equation was derived assuming that the diffusion of SO_2 from the bulk of the flue gas to the solid-gas interface is the rate controlling step of the overall reaction of SO_2 and paper.

The assumption is also made that an equilibrium condition exists between the SO_2 at the solid-gas interface and the SO_2 in the paper and that this condition can be expressed by the relationship

$$C_i = HC_p$$

Substituting in (3)

$$k_g a (C_G - HC_p) = \rho \frac{\partial C_p}{\partial t} \qquad (4)$$

Rearranging (4) in terms of X and Y

$$\frac{\partial x}{\partial t} = \frac{k_g a C_o}{\rho Q} Y - \frac{k_g a H}{\rho} X \qquad (5)$$

Several boundary and initial conditions were added to complete the technical model. If the composition of the entering flue gas is maintained constant

$$Y = 1 \text{ for } Z = 0,\ t \geq 0$$

Also, no change in SO_2 concentration will occur at any point in the packed bed until the entering flue gas has had time to flow down to that point. This condition can be expressed as

$$Y = 0 \text{ for } Z > 0,\ t \geq \frac{\epsilon}{L} Z$$

$$X = 0 \text{ for } Z > 0,\ t \geq \frac{\epsilon}{L} Z$$

where the paper initially has been assumed to have essentially zero SO_2 concentration. By specifying the height of the column (Z_{final}) and the maximum allowable SO_2 mole fraction in the exit flue gas (Y_{final}), the final boundary becomes

$$Y \leq Y_{final} \text{ at } Z = Z_{final},\ \epsilon > 0$$

Equations (2) and (5) along with the above conditions completely define the transient behavior of the fixed-bed sorption column. Solution of this protion of the mathematical model will yield concentration of SO_2 in either the gas or solid phase for any Z or t.

The economic portion of the model estimates the capital and operating costs of the proposed process. The cost-capacity values used to determine the total plant capital cost were obtained by curve fitting data provided in "Cost Engineering in the Process Industries," C. H. Chilton, 1960. All costs were updated to 1968 using the ENR Index and multiplied by their appropriate installation cost factors. For example the equation for determining the sorption column cost is:

$$COLCST = (2.515 \times 10^{-6} D^4 - 8.99 \times 10^{-4} D^3 + 0.1182 D^2 - 1.079 D + 82.09)\ Z_{final} \times 2.93 \times 2$$

where

COLCST = installed cost of a single tower

D = tower diameter in inches

Z_{final} = tower height in feet

2.93 = updating factor

2.0 = installation factor

The operating costs are calculated assuming that the SO_2 recovery system requires two operators per shift and three shifts per day.

3.2.2 Method or Computer Solution

The mathematical model was translated into a FORTRAN II computer program which was then utilized to determine cost and operational sensitivities of various independent parameters. A description of the method used to obtain a solution to the technical portion of the model, comprised of Equation (3) and (5) along with the corresponding initial and boundary conditions is given below.

Equation (3) can be simplified by the change of variables:

$$S = (\epsilon/L)Z \rightarrow \frac{\partial S}{\partial Z} = \frac{\epsilon}{G}$$

$$\theta = t - \left(\frac{\epsilon}{G} Z\right) \rightarrow \frac{\partial \theta}{\partial t} = 1$$

$$\frac{\partial \theta}{\partial Z} = -\frac{\epsilon}{G}$$

then

$$\frac{\partial Y}{\partial Z} = \frac{\partial Y}{\partial S}\frac{\partial S}{\partial Z} + \frac{\partial Y}{\partial \theta}\frac{\partial \theta}{\partial Z}$$

$$= \frac{\partial Y}{\partial S}\frac{\epsilon}{G} - \frac{\partial Y}{\partial \theta}\frac{\epsilon}{G}$$

and

$$\frac{\partial Y}{\partial t} = \frac{\partial Y}{\partial \theta}\frac{\partial \theta}{\partial t} + \frac{\partial Y}{\partial t}\frac{\partial S}{\partial t}$$

$$= \frac{\partial Y}{\partial \theta}$$

Similarly,

$$\frac{\partial x}{\partial t} = \frac{\partial X}{\partial \theta}$$

Substituting the above into Equation (3) and (5) yields

$$\frac{\epsilon}{G}\frac{\partial Y}{\partial S} - \frac{\epsilon}{G}\frac{\partial Y}{\partial \theta} + \frac{\epsilon}{G}\frac{\partial Y}{\partial \theta} + \frac{\rho Q}{GC_o}\frac{\partial X}{\partial \theta} = 0$$

which simplifies to

$$\frac{\partial Y}{\partial S} + \frac{\rho Q}{\epsilon C_o} \frac{\partial X}{\partial \theta} = 0 \qquad (6)$$

and

$$\frac{\partial X}{\partial \theta} = \frac{k_g a C_o}{\rho Q} Y - \frac{k_g a H}{\rho} X \qquad (7)$$

The boundary conditions become

$$Y = 1 \text{ at } S = 0 \qquad \theta \geq 0$$
$$Y = 0 \text{ at } \theta = 0 \qquad S > 0$$

$$Y \leq Y_{final} \qquad \text{at } S = S_{final} \qquad \theta > 0$$
$$X = 0 \qquad \text{at } \theta = 0 \qquad S \geq 0$$

Equations (6) and (7) were solved on a SDA 940 computer using a finite difference approach known as the "modified Euler's method" or "Henn's first method" (36). The program pertaining to the technical model was written so that the following parameters could be varied:

- cross-sectional area of the column
- height of column
- average column pressure
- average column temperature
- flue gas flow rate at standard conditions (1 atm, 60°F)
- mole fraction of SO_2 in feed flue gas
- maximum allowable residual SO_2 mole ratio in exit flue gas, Y_{final}
- saturated SO_2 concentration on paper, Q
- weight of paper per unit column volume, ρ
- void fraction of the column, ϵ
- mass transfer coefficient, $k_g a$
- equilibrium constant, H

The technical program outputs the batch time and the total moles of SO_2 which are sorbed on the paper during one batch. The time at which the mole fraction of SO_2 in the exit flue gas exceeds the specified maximum allowable SO_2 mole fraction determines the batch time. Since the moles of SO_2 sorbed on the paper at each sub-interval of height is know, the total moles of SO_2 are calculated by using Simpson's rule to integrate over the height of the column.

The computer program for the economic model allowed the following parameters to be varied:

- paper cost
- SO_2 credit value
- heat credits

The output form the economic portion of the model includes:

- total plant capital cost
- hourly operating cost
- hourly SO_2 credit
- hourly paper credit
- yearly paper usage
- yearly amounts of SO_2 recovered
- total plant yearly cost

3.3 PROCESS BASE CASE CONDITIONS

A study of the proposed SO_2 recovery system was conducted specifically for the case in which cellulose (paper) is the organic solid employed. Each of the technical and economic variables of the computer program was assigned a value, either from known experimental data or from best estimates of parameter, for the base case of operation. References relating to the base conditions are given when possible.

The selected base conditions are:

1. Column diameter = 30 feet
2. Column height, Z_{final} = 60 feet
3. Average pressure in column, P = 14.9 psi
4. Average temperature in column, T = 300°F
5. Flue gas flow rate at standard conditions (1 atm, 60°F) = 87.3 million cubic feet per hour[1]
6. Mole fraction of SO_2 in feed flue gas = 0.003 (4)
7. Maximum allowable residual SO_2 mole ratio in exit flue gas, Y_{final} = 0.1 mols SO_2 leaving column per mole SO_2 in feed (3)
8. Saturated SO_2 concentration on paper, Q = 0.1 lb SO_2/lb paper (5)

[1]The flue gas flow rate corresponds to an 800-megawatt power plant burning 280 tons coal/hour (37).

9. Weight of paper per unit column volume, ρ = 7 lbs paper/ft^3 column[1]
10. Void fraction of column, ϵ = 0.1 actual volume/column volume[1]
11. Mass transfer coefficient, $k_g a$ = 20,000 moles/(hr)(ft^3 column) (moles/ft^3)
12. Equilibrium constant, H = 0.001 $\frac{\text{moles } SO_2/ft^3 \text{ gas}}{\text{moles } SO_2/\text{lb paper}}$
13. Cost of paper = 0.3 cents/lb (Reference 5)
14. Credit for SO_2 recovered = 0.5 cents/lb SO_2[2]
15. Heat credit = 50 cents/MM Btu (37, 38).

Two percent of the paper in the column is replaced after each sorption run. The percentage is low, because as paper replacement increases, it becomes exceedingly more difficult to provide an adequate amount of paper to supply the power plant. The heat of combustion attributed to the spent paper is 7560 Btu/lb paper.

The power plant is assumed to burn 280 tons of 4% sulfur coal per hour and to operate at 90% efficiency (330 days/yr). Essentially all of the SO_2 sorbed is removed from the paper during the regeneration step.

The heat required to desorb the SO_2 from the paper was assumed to be of the same order of magnitude as the SO_2 heat of solution in water, and by using this value and a heat cost of 50 cents/MM Btu, the cost of regenerating the paper was estimated at approximately 0.01 cents/lb SO_2. Since the cost of regenerating the paper would have little effect on the SO_2 credit value (0.5 cents/lb SO_2 in the base case), it was assumed negligible.

The SO_2 credit value represents the net worth of the SO_2 as a raw material feed gas. It does not include the cost of converting the SO_2 to a marketable product (i.e., sulfuric acid).

[1]The density of paper was considered a constant at 70 lbs/ft^3 (39).

[2]The SO_2 credit was evaluated based on a 100% sulfuric acid selling price of $20/ton (1.5 cents/lb SO_2). It is equated to the market value of 1.5 cents/lb SO_2 less the cost of upgrading the SO_2 to sulfuric acid.

PROCESS COSTS FOR BASE CONDITIONS

The computer simulation of the cellulose-SO_2 recovery system operating at the base conditions described previously produced the following results:

- Batch time = 0.51 hours
- Paper usage = 46,200 tons/year
- SO_2 recovered = 162,600 tons/year
- Total capital cost = $2,770,000
- Operating Profit = $119/hour
  $0.42/ton coal
  $941,000/year

3.4 RESULTS OF PARAMETRIC ANALYSIS

Figures 5 through 29 show the results of the parametric analysis of the paper-SO_2 recovery system conducted by perturbing a selected parameter while maintaining all other variables in the base case conditions. In Figures 7 through 21, the following variables

- Mass transfer coefficient - $k_g a$
- Equilibrium constant - H
- Column diameter
- Column height
- Weight of paper per unit column volume (ρ) - void fraction (ϵ)[1]
- Mole fraction of SO_2 in feed flue gas
- Saturated SO_2 concentration on paper, Q

were plotted as functions of sorption batch time and as functions of operating profits. The operating profit in terms of MM $/yr is calculated assuming that the power plant operates at 90% efficiency (330 days/yr) and the operating profit in $/ton coal assumes that the power plant burns 280 tons coal/hr. The curves are constructed for SO_2 credit values of 1.0 cents/lb and 0.5 cents/lb.

[1] If the density of paper (DEN) is constant, the weight of paper per unit column volume (ρ) and the column void fraction (ϵ) are related by the expression:

$$DEN = \rho/(1 - \epsilon)$$

Figures 22 and 23 show the effects of column diameter and height on the overall capital costs of the SO_2 recovery system. Figure 24 illustrates the effect of the paper cost on the operating profit of the system. Figures 25 and 26 are graphs of the system's operating profit vs the percentage of paper makeup per sorption cycle, plotted for two SO_2 credit values and two heat credit values. Figure 27 is a plot of the operating profit vs the SO_2 credit value and Figure 28 shows the operating profit as a function of the heat credit value.

Figure 29 is a plot showing the effects of a general sorbent cost in $/hr on the operating profits of the system. Since the heat credit was assumed zero in the construction of this plot the curves apply to a sorbent which is discarded after releasing the sorbed SO_2.

When applicable, the value of the base case is indicated on the figure. A description of each of the graphs follows.

Figure 7

This plot shows the SO_2 sorption batch time in hours vs the mass transfer coefficient, $k_g a$, in units of moles/(hr)(ft^3 column) (moles/ft^3). The $k_g a$ range extends from 10,000 to 70,000. All other variables were at their respective base case conditions.

Figure 8

The effects of a variance in $k_g a$ on the operating profit of the recovery system is shown in this figure. The range of $k_g a$ is 10,000 to 70,000 moles/(hr)(ft^3 column) (moles/ft^3) and the base case $k_g a$ is 20,000. Curves are plotted for SO_2 credit values of 0.5 cents/lb and 1.0 cents/lb.

Figure 9

In this figure, the SO_2 sorption batch time is plotted against the solid-gas interfacial equilibrium constant (H). The equilibrium constant is defined by the expression

$$C_i = HC_p$$

where C_i is the SO_2 concentration at the fluid-solid interface which is in equilibrium with C_p, the moles of SO_2 per lb of paper. The units for this constant are (moles SO_2/ft^3 gas)/(moles SO_2/lb paper).

The batch time was evaluated for H values ranging from 10^{-2} to 10^{-5} and, as shown, the batch time increases as the value of H decreases in magnitude. All other variables were at base case conditions.

Figure 10

This figure is a plot of the equilibrium constant, H, vs operating profit in terms of MM $/yr and $/ton coal. The base case condition in 0.001 (moles SO_2/ft^3 gas)/(moles SO_2/lb paper).

Figure 11

The effect of sorption column diameter on the SO_2 sorption batch time is illustrated in Figure 11. As expected, the batch time increases as the column diameter becomes larger. The base case diameter is 30 ft.

Figure 12

Figure 12 shows the effect of column diameter on the overall operating profit of the SO_2 recovery system. Curves are plotted for SO_2 credit value of 1.0 cents/lb and 0.5 cents/lb. All other values are at the base case operating conditions.

For the proposed SO_2 recovery system, the batch time decreases as the column height becomes smaller (Figure 11) but the amount of paper required by the sorption process becomes larger. Because the fuel credit value exceeds the initial cost, rising operating profits are realized as the amount of paper burned for fuel increases. Therefore, a trade-off results for, although the shorter column returns a larger margin of profit, problems related to obtaining a sufficient supply of paper and to regenerating the paper in the given time period will likely arise.

Figure 13

Figure 13 shows the effect of column height on the sorption batch time for columns having diameters of 30 feet and 40 feet. Besides indicating that batch time increases proportionately with column height, the plot also shows that the rate of increase in batch time (represented by the slope of the curves) is greater for the column 40 feet in diameter.

Figure 14

The effect of column height on the operating profit for a column 30 feet in diameter is shown in this figure. As shown, the operating profit decreases as the column height increases. With the substitution of column height for column diameter, the discussion presented for Figure 8 would also apply here.

Figure 15

This plot is similar to Figure 14 except that the curves correspond to a column 40 feet in diameter.

Figure 16

The effect of the weight of paper per cubic foot of column and void fraction (ft^3 actual volume/ft^3 empty column) on the sorption batch time is illustrated in Figure 16. The density of the paper (lbs paper/ft^3 paper) is assumed constant and thus the weight of paper per cubic foot of column and the fraction (values in parentheses) are related by

$$DEN = \rho/(1 - \epsilon)$$

when

DEN = lb./paper/ft^3 paper

ρ = lb paper/ft^3 column

ϵ = ft^3 actual volume/ft^3 empty column

As expected, the batch time increases as the amount of paper in the column increases.

Figure 17

Operating profit vs the weight of paper per cubic foot of column and void fraction are plotted in Figure 17. The numbers in parentheses along the abscissa of Figure 17 represent values for the void fraction. According to the plot, the weight of paper per unit column volume (and the void fraction) does not significantly affect the operating profit over the range analyzed.

Figure 18

Figure 18 shows the effect of the mole fraction of SO_2 in the flue gas being fed to the sorption column on the sorption batch time. As can be

seen from the curve, the mole fraction of SO_2 in the feed flue gas has a significant effect on the batch time.

Figure 19

This is a plot of the mole fraction of SO_2 in feed flue gas vs the operating profit. The operating profits do increase as the SO_2 feed mole fraction becomes larger because the revenue from SO_2 recovery also increases. Although the operating profits improve with a high SO_2 mole fraction in the feed flue gas, batch time favors a low value for this parameter.

Figure 20

In Figure 20, the SO_2 sorption batch time is shown to increase as the SO_2 concentration of the paper (lbs SO_2/lb paper) at saturation conditions also increase.

Figure 21

Figure 21 illustrates curves relating the saturated SO_2 concentration of the paper to the operating profit of the proposed system. Again, the operating profits are highly dependent on the SO_2 credit value.

Figure 22

Figure 22 indicates the effect of an increase column diameter on the capital investment of the proposed SO_2 recovery process. All parameters, except column diameter, were at their respective base conditions.

Figure 23

The effect of column height on overall capital investment is shown in this figure. Two curves corresponding to the column diameters of 30 feet and 40 feet are plotted.

Figure 24

Figure 24 shows the inversely proportional relationship between the operating profit of the proposed SO_2 recovery process and the cost of paper. According to the plot, a process operating at the base case conditions will show a profit if the paper cost is less than 1.3 cents/lb.

Figure 25

This figure is a plot of the operating profit vs the percentage of paper replacement per sorption cycle. In the base case, 2% of the paper is replaced prior to SO_2 sorption. As the percentage of paper replacement increases, the practical problem of obtaining and handling sufficient amounts of paper becomes magnified. The slopes of the curves are positive because the base case operating conditions result in a paper fuel credit that exceeds the paper cost.

Figure 26

Figure 26 is similar to Figure 25 except that the heat credit has been altered from the base case condition of 50 cents/MM Btu to 25 cents/MM Btu. In this case, the fuel credit of the paper no longer exceeds the initial cost of the paper, and therefore the slopes of the curves are negative. If all other parameters except the heat credit are at their base case values, the proposed process will show a profit if the paper replacement per sorption cycle is less than 16%. The curves in both Figures 21 and 22 were calculated using 7560 Btu/lb paper as the heat of combustion of paper.

Figure 27

Figure 27 illustrates the effect of the SO_2 credit value on the operating profit of the SO_2 recovery system. The SO_2 credit value represents the net worth of SO_2 as a raw material fuel gas but does not include the cost of converting it to a salable product (i.e., sulfuric acid). A process operating at the base-case conditions will operate at a profit if the SO_2 credit value is greater than 0.2 cents per pound. If 100% sulfuric acid can be marketed at $20/ton (1 cent/lb of sulfuric acid or 1.5 cents/lb of SO_2), a profit can be realized if the cost of upgrading the SO_2 to sulfuric acid is less than 1.3 cents/lb of SO_2 (assuming all of the SO_2 sorbed on the paper is converted to sulfuric acid.

Figure 28

This figure is a plot of the heat credit value (cents/MM Btu) vs the operating profit. These curves are for the base case condition in which 2% of the paper in the column is used as fuel during each sorption cycle. The slope of the curve would increase if the percentage of paper replacement

per sorption cycle was increased. The values of the operating profit were calculated assuming that the heat of combustion of paper is 7560 Btu/lb.

Figure 29

The curves in Figure 29 apply to a SO_2 recovery system employing a general sorbent material but otherwise similar to the proposed system. In this graph, the operating profit is plotted as a function of sorbent cost ($/hr). Zero heat credit was given to the sorbent in determining the curves and, therefore, the sorbent cost applies directly to a material which is discarded upon replacement. If the spent sorbent does have some economic worth, the value on the abscissa corresponds to the difference between the initial cost of the sorbent and any credit which can be assigned to the spent sorbent.

3.5 CONCLUSIONS

The results of the preliminary chemical systems analysis demonstrate that the proposed cellulose - SO_2 recovery process is economically feasible. Specifically the analysis computed that the process, operating at the selected base case conditions, will show a profit of $941,000 per year (42 cents/ton coal). This is a preliminary analysis of the proposed system and a more thorough determination of the values of the process parameters (probably by laboratory experimentation) is needed to substantiate these results.

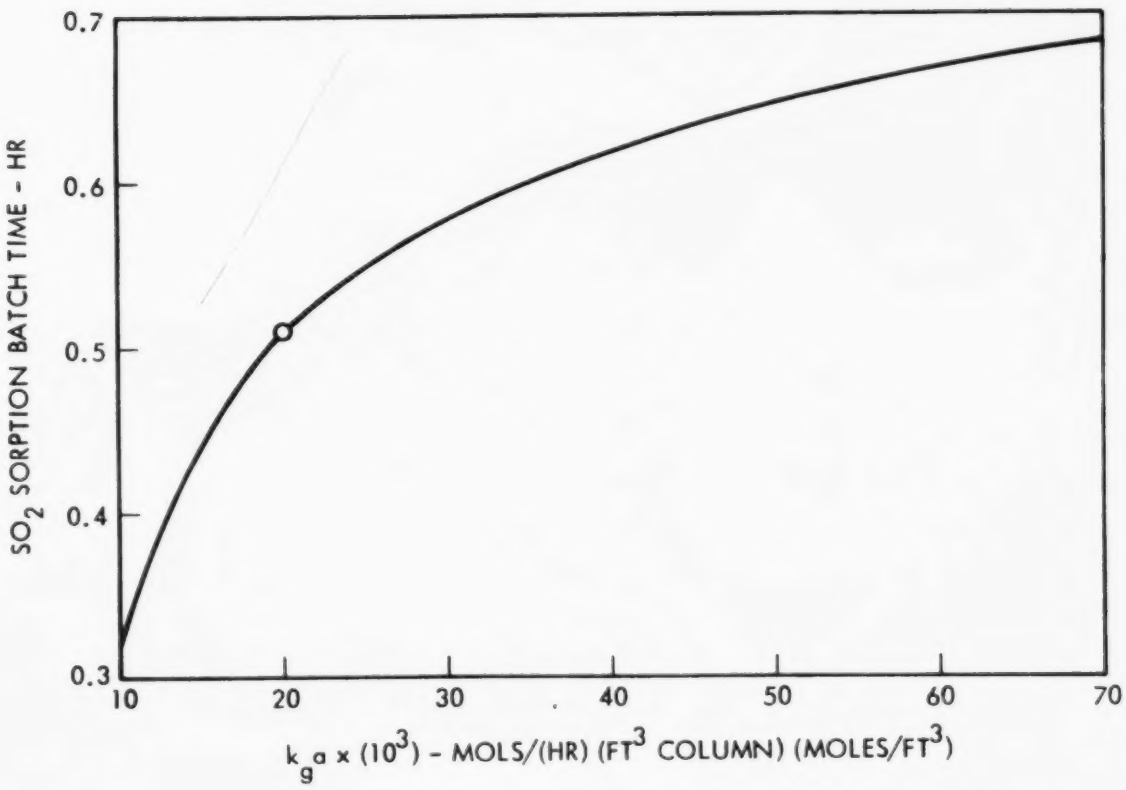


Figure 7. Effect of the Mass Transfer Coefficient on the SO_2 Sorption Batch Time

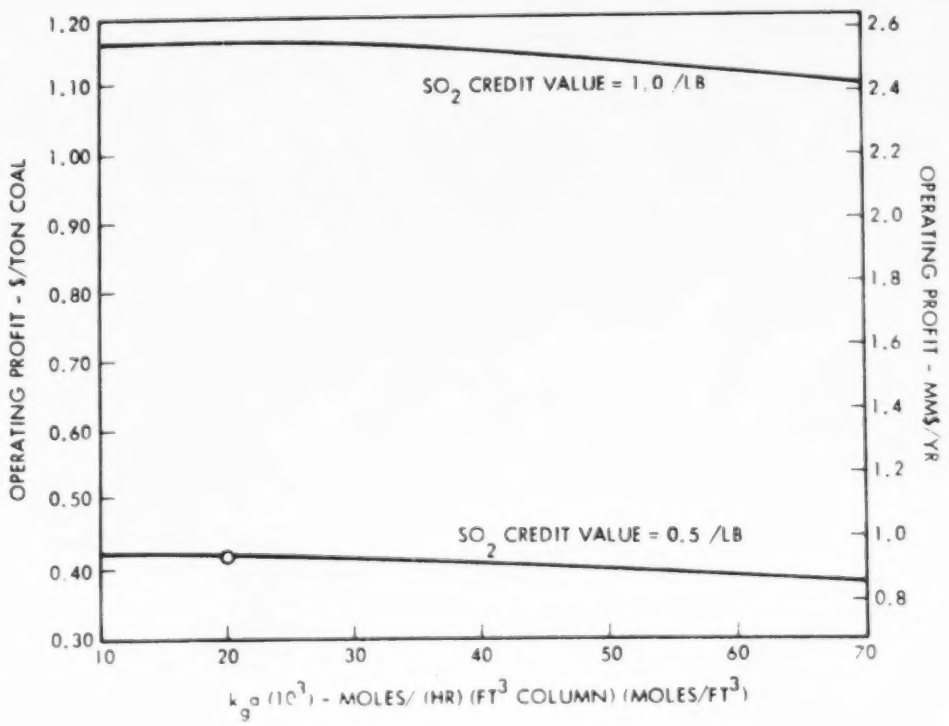


Figure 8. Effect of the Mass Transfer Coefficient on the Operating Profit of the SO_2 Recovery System

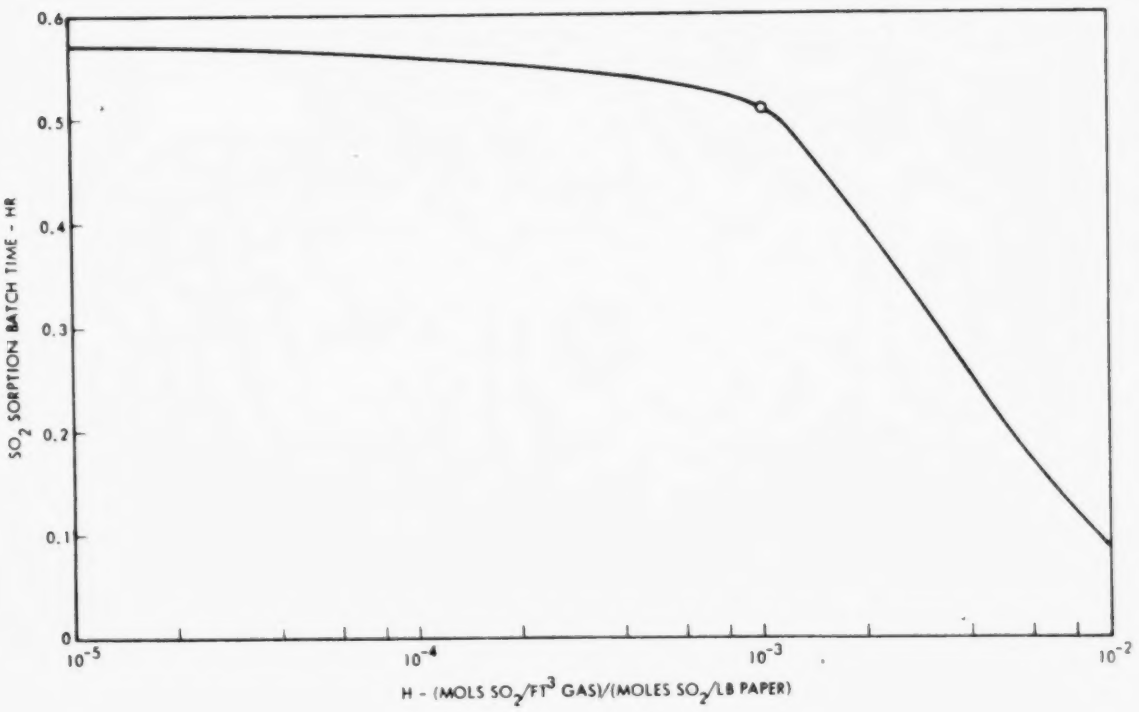


Figure 9. Effect of the Gas-Solid SO_2 Equilibrium Constant on the SO_2 Sorption Batch Time

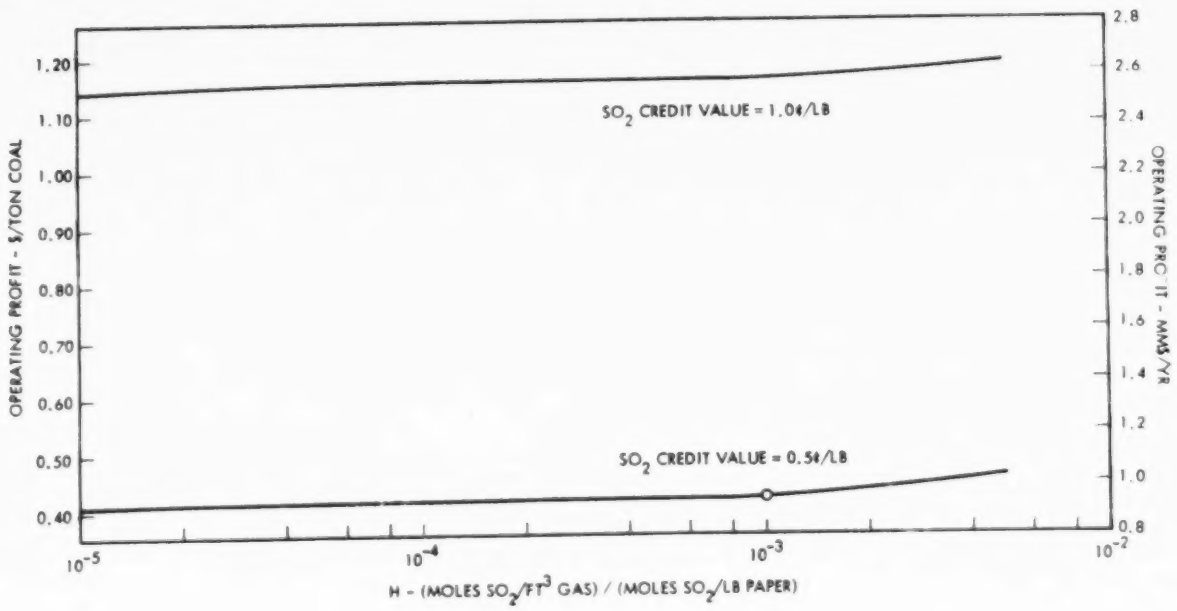


Figure 10. Effect of the Gas-Solid SO_2 Equilibrium Constant on the Operating Profit of the SO_2 Recovery System

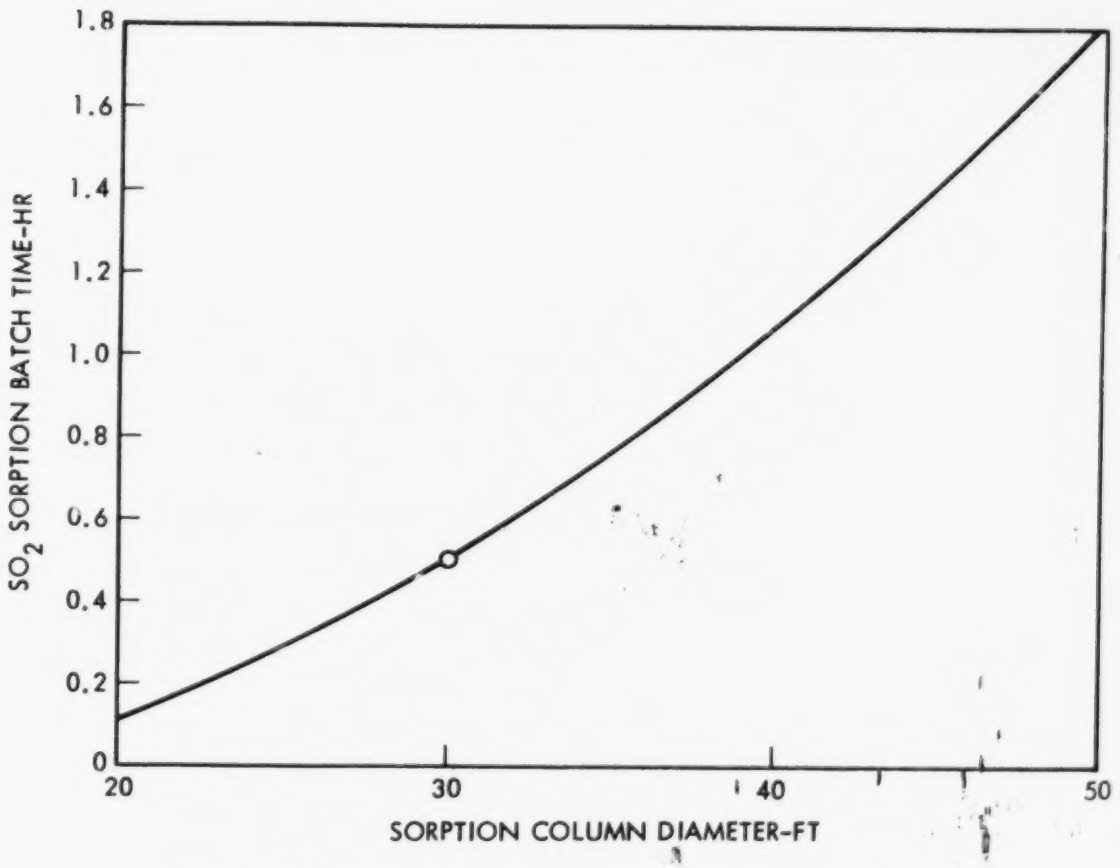


Figure 11. Effect of Sorption Column Diameter on the SO_2 Sorption Batch Time

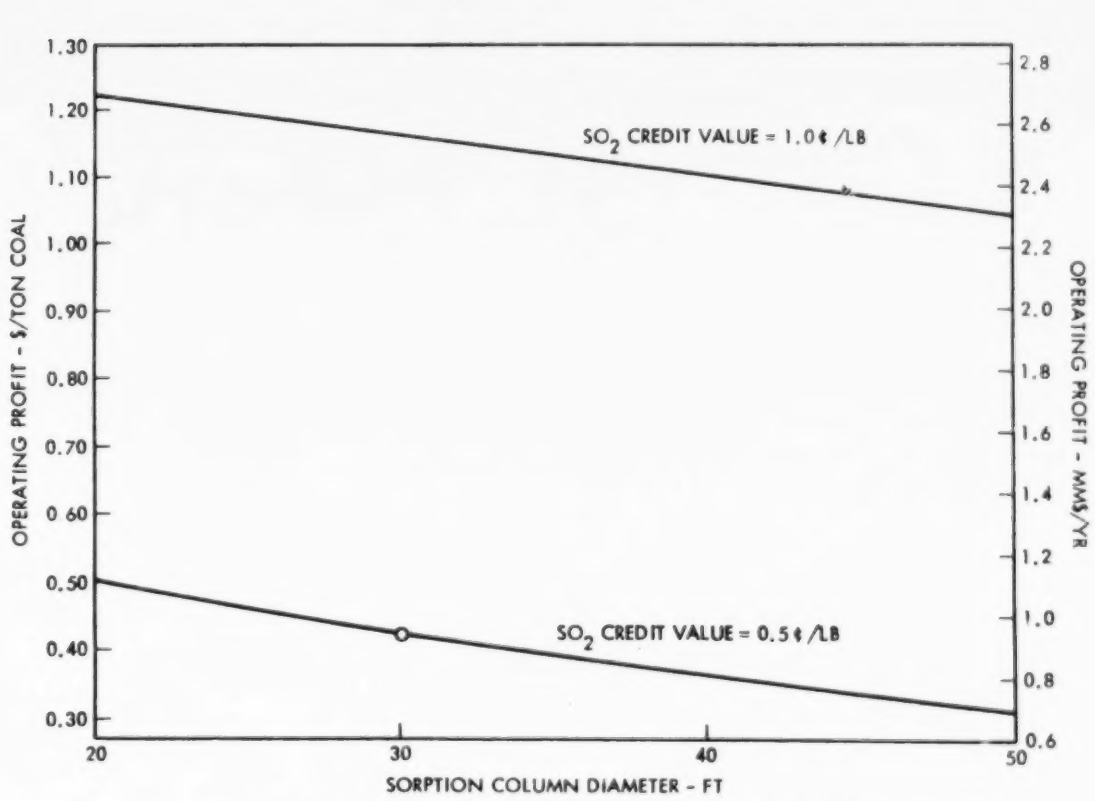


Figure 12. Effect of the Sorption Column Diameter on the Operating Profit of the SO_2 Recovery System

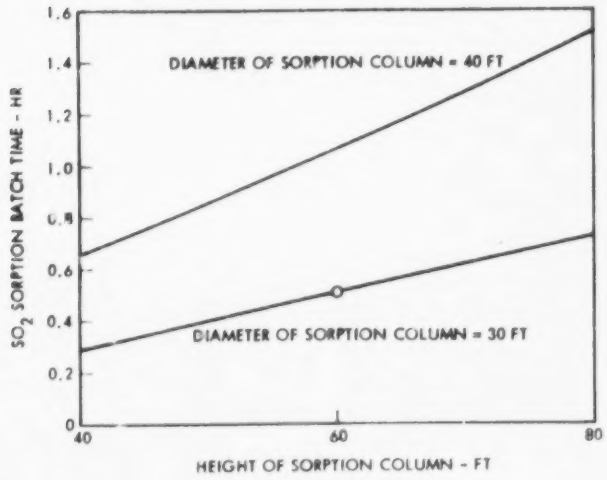


Figure 13. Effect of Sorption Column Height on the SO_2 Sorption Batch Time

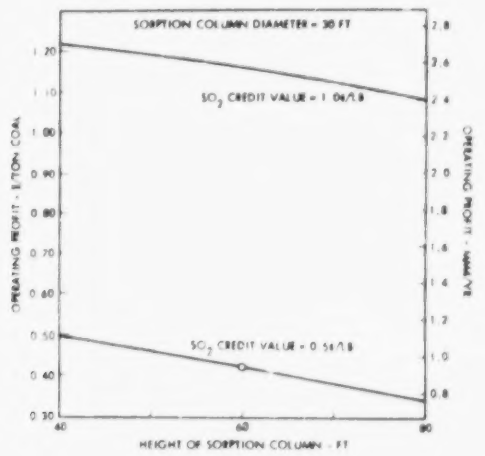

SORPTION COLUMN DIAMETER = 30 FT
SO_2 CREDIT VALUE = 1.04/LB
SO_2 CREDIT VALUE = 0.56/LB
OPERATING PROFIT - $/TON COAL
OPERATING PROFIT - MM$/YR
HEIGHT OF SORPTION COLUMN - FT

Figure 14. Effect of the Sorption Column Height on the Operating Profit of the SO_2 Recovery System (30-ft. col.)

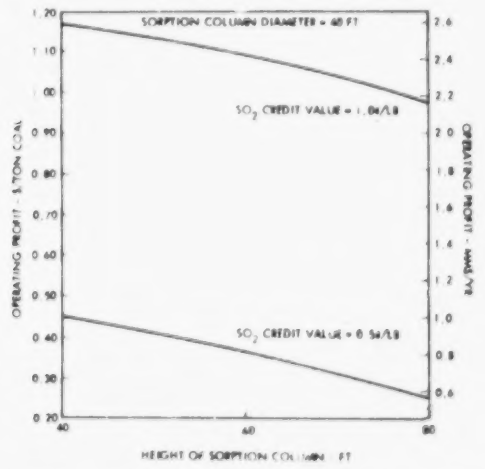

SORPTION COLUMN DIAMETER = 40 FT
SO_2 CREDIT VALUE = 1.04/LB
SO_2 CREDIT VALUE = 0.56/LB
OPERATING PROFIT - $/TON COAL
OPERATING PROFIT - MM$/YR
HEIGHT OF SORPTION COLUMN - FT

Figure 15. Effect of the Sorption Column Height on the Operating Profit of the SO_2 Recovery System (40-ft. col.)

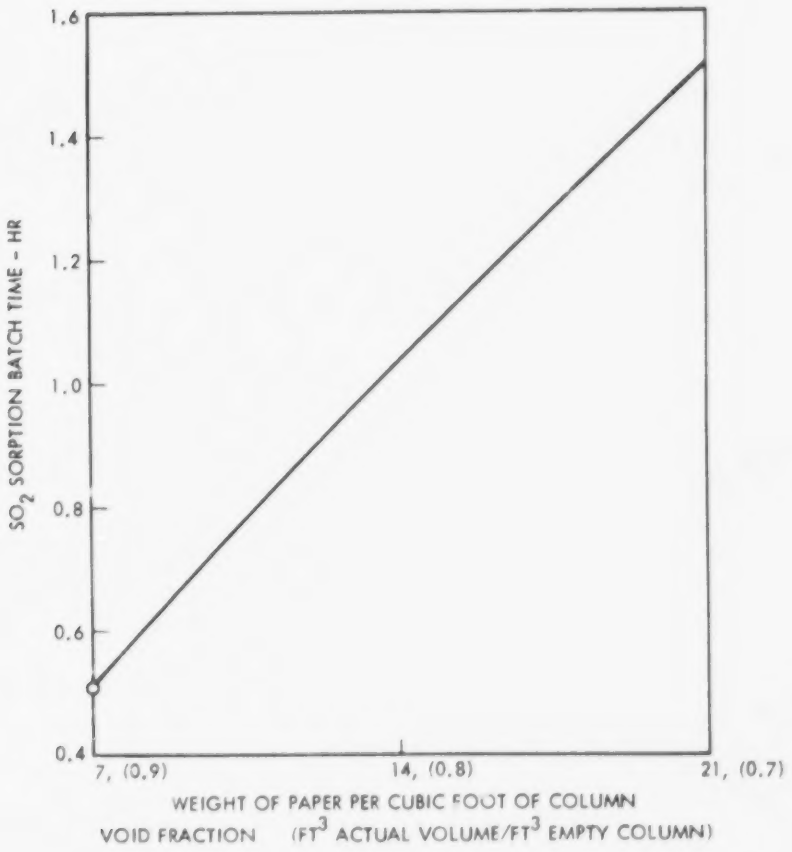


Figure 16. Effect of the Weight of Paper per Cubic Foot of Column and the Column Void Fraction on the SO_2 Sorption Batch Time

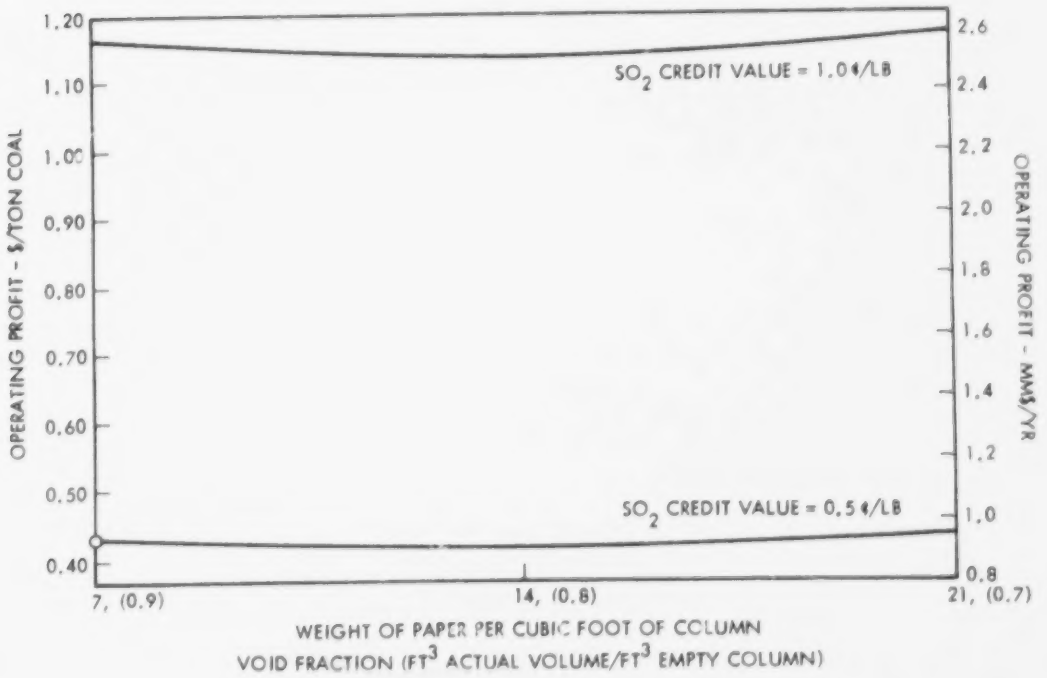


Figure 17. Effect of the Weight of Paper per Cubic Foot of Column and the Column Void Fraction on the Operating Profit of the SO_2 Recovery System

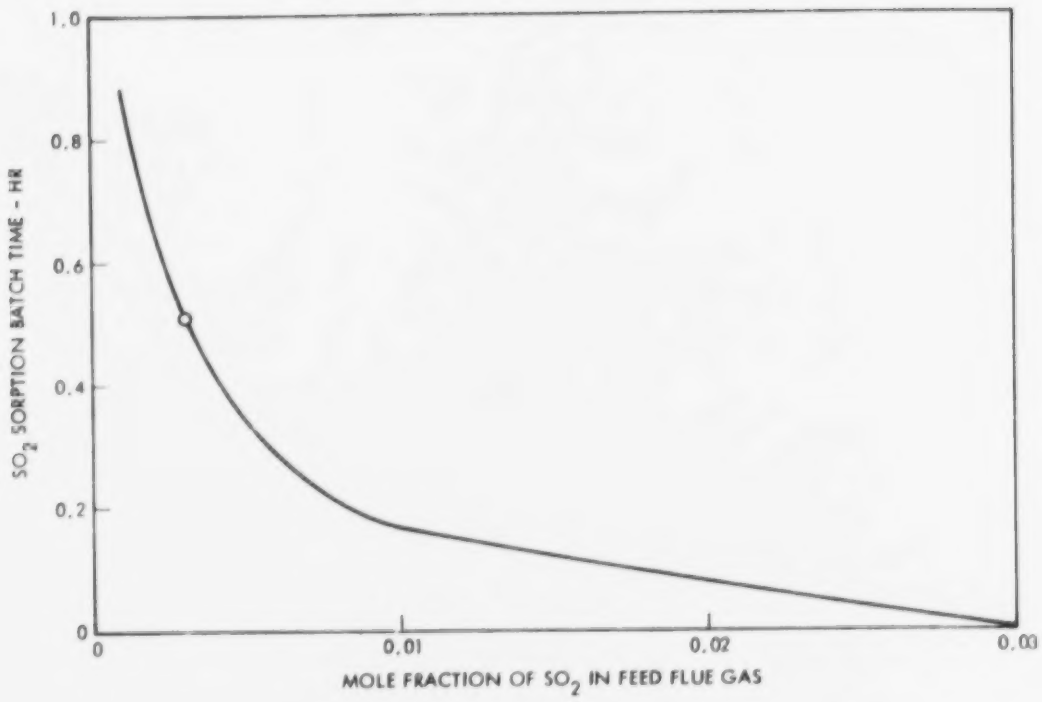


Figure 18. Effect of the SO_2 Mole Fraction in the Feed Flue Gas on the SO_2 Sorption Batch Time

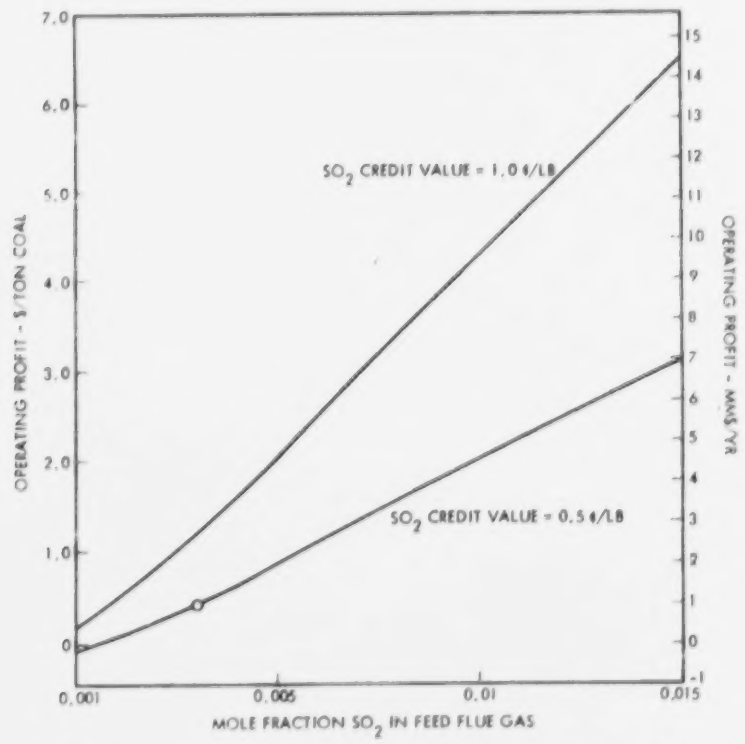


Figure 19. Effect of the SO_2 Mole Fraction in the Feed Flue Gas on the Operating Profit of the SO_2 Recovery System

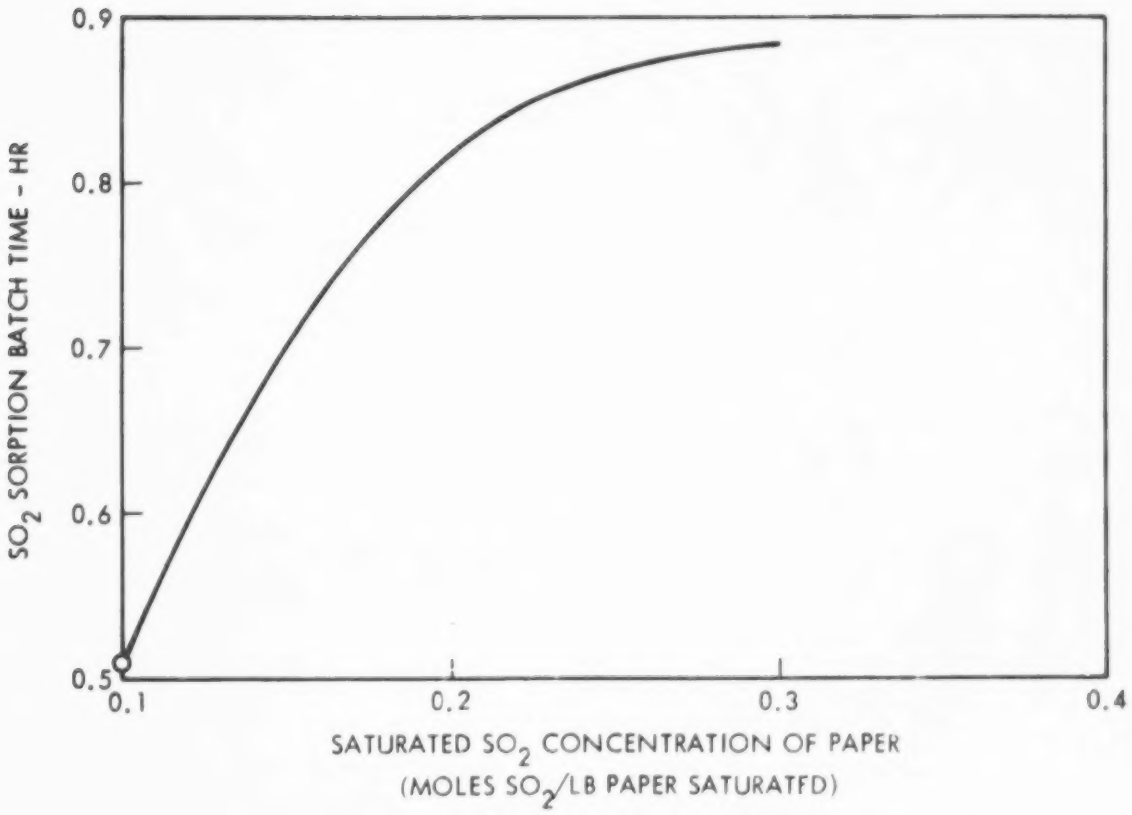


Figure 20. Effect of the SO_2 Concentration of the Paper at Saturation on the SO_2 Sorption Batch Time

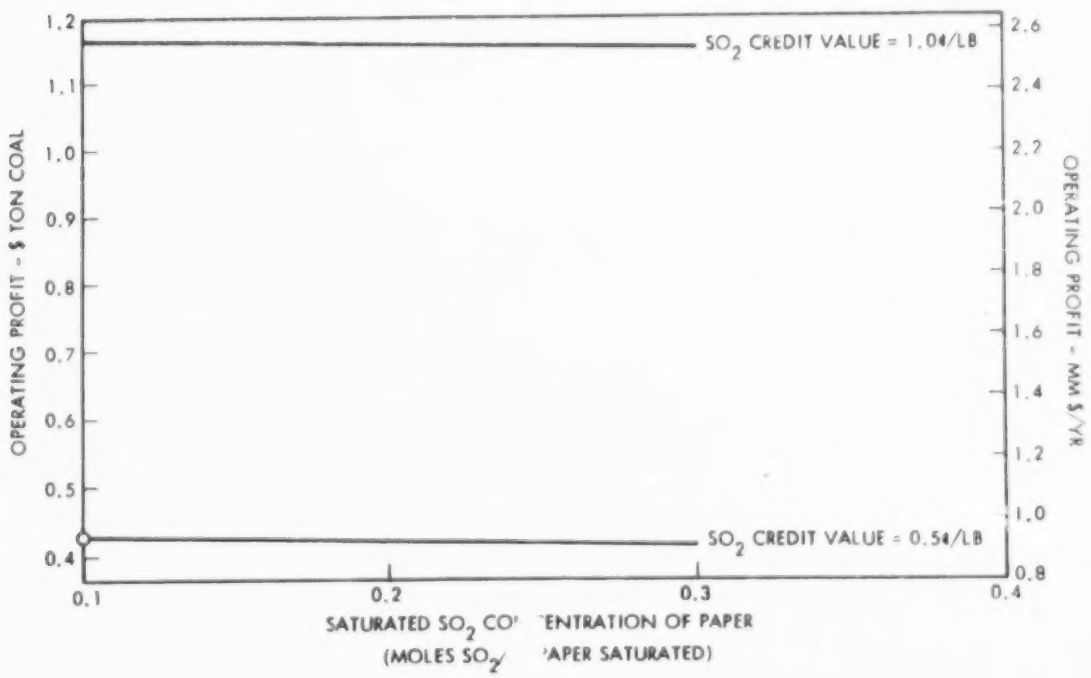


Figure 21. Effect of the SO_2 Concentration of the Paper at Saturation On the Operating Profit of the SO_2 Recovery System

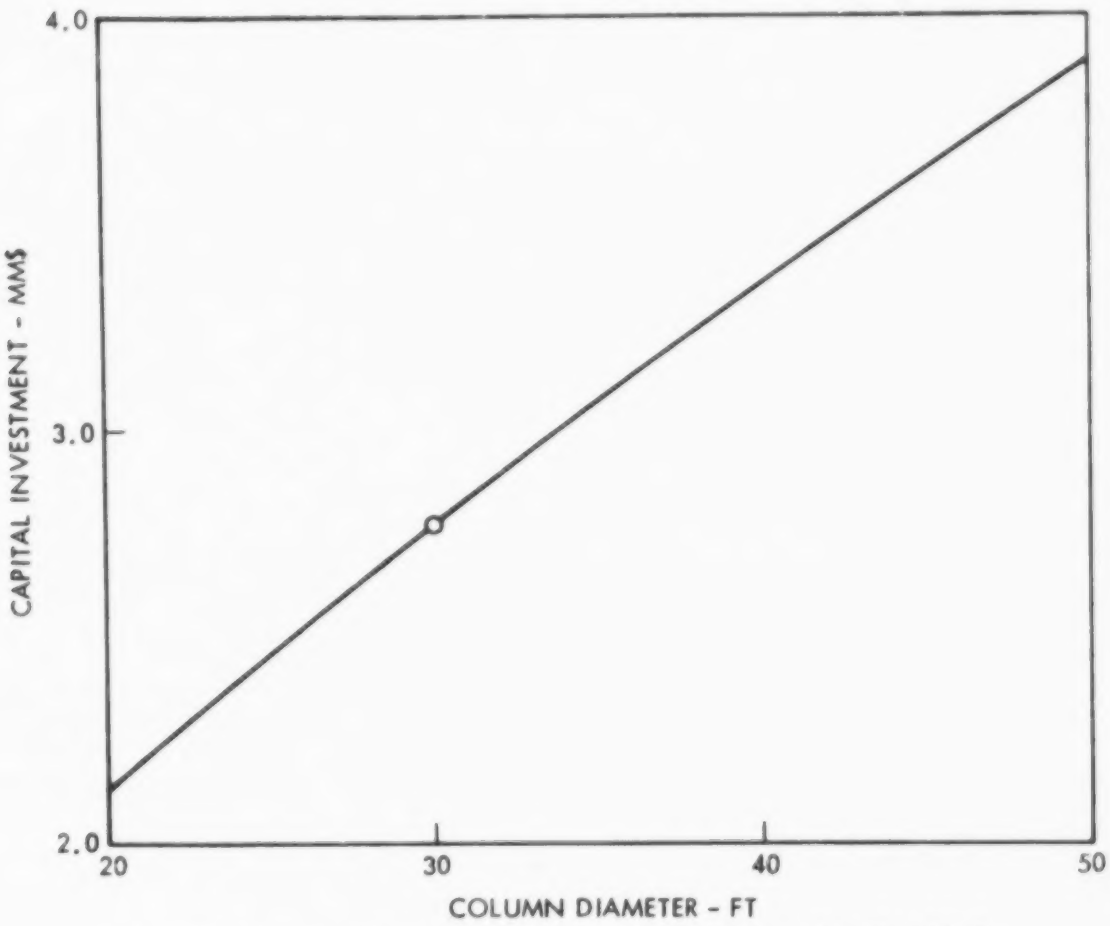


Figure 22. Effect of Column Diameter on the Capital Investment for the SO_2 Recovery System

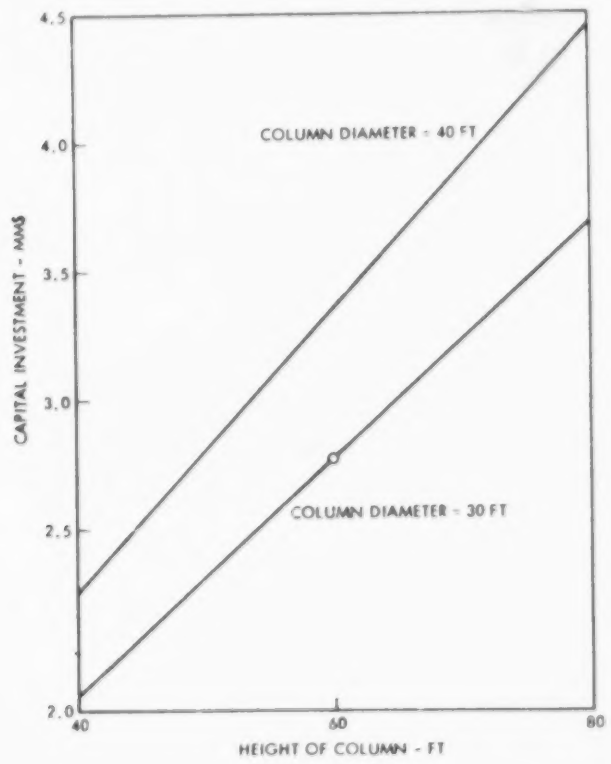


Figure 23. Effect of Column Height on the Capital Investment for the SO_2 Recovery System

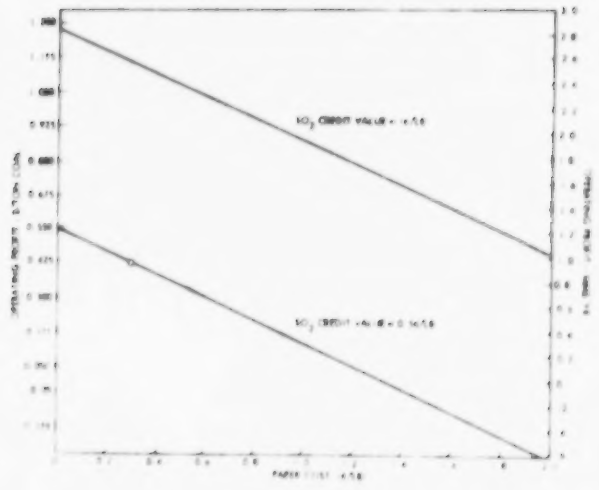


Figure 24. Effect of the Cost of Paper on the Operating Profit of the SO_2 Recovery System

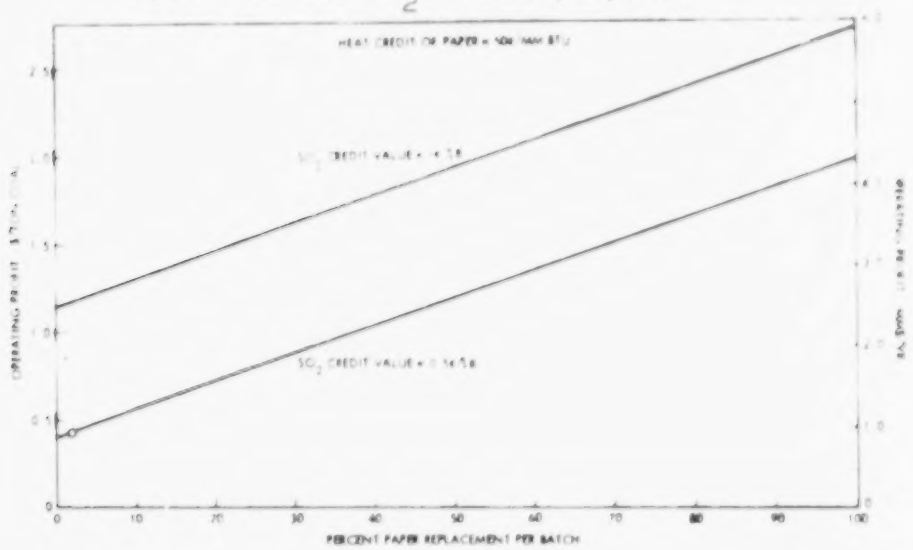


Figure 25. Effect of the Paper Replacement per Batch on the Operating Profit of the SO_2 Recovery System

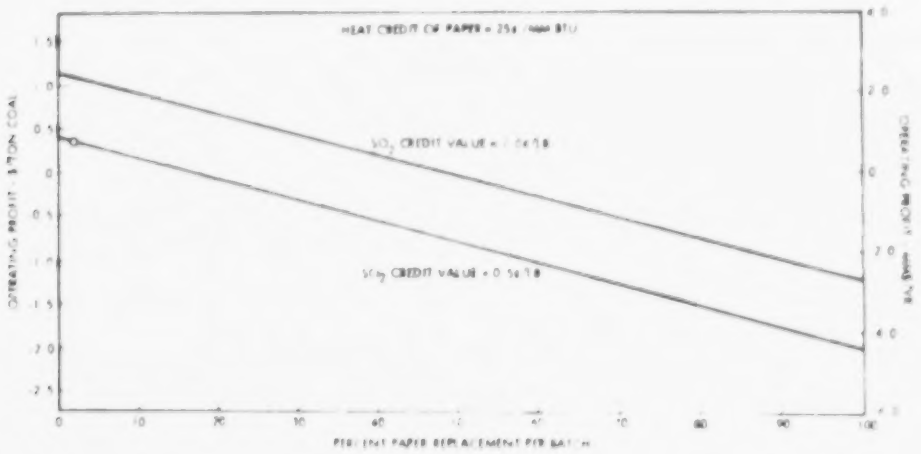


Figure 26. Effect of the Paper Replacement per Batch on the Operating Profit of the SO_2 Recovery System (Heat Credit Altered)

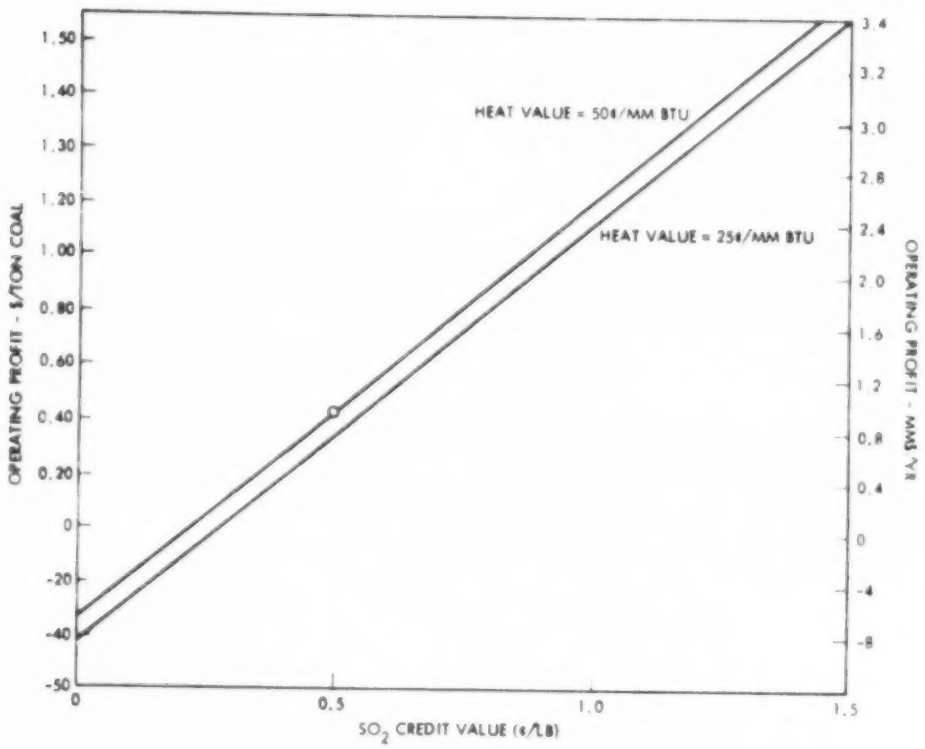


Figure 27. Effect of the SO_2 Credit Value on the Operating Profit of the SO_2 Recovery System

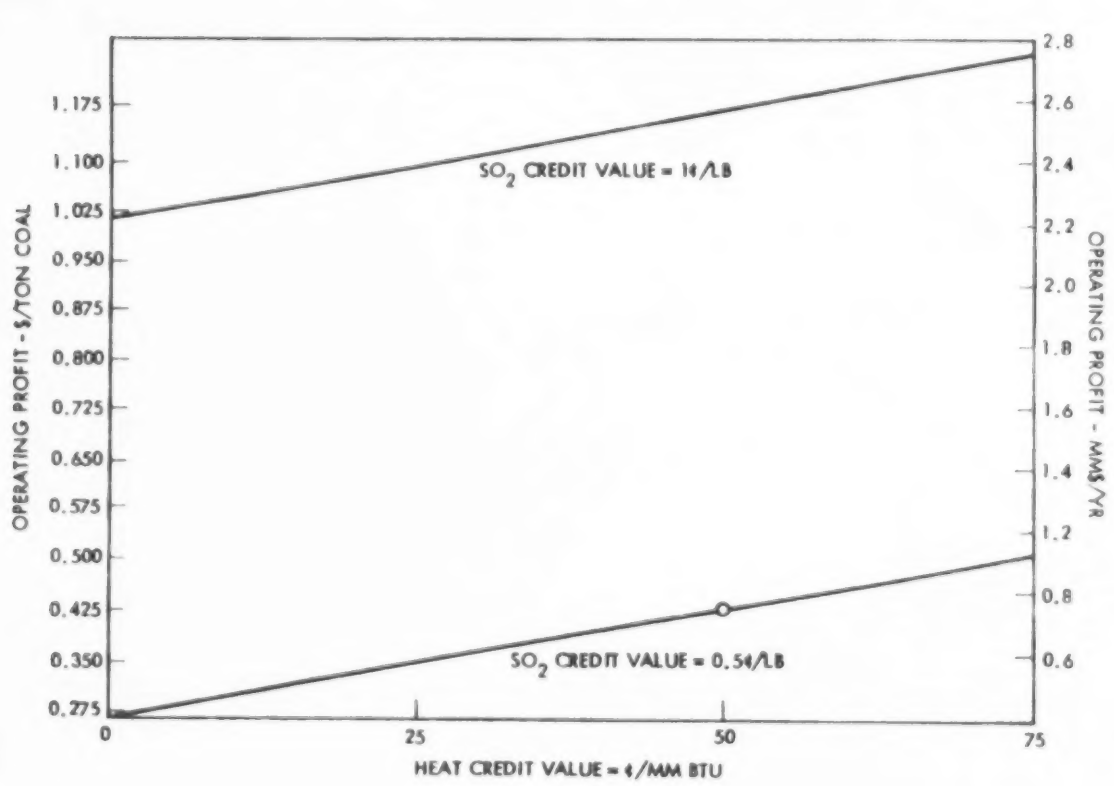


Figure 28. Effect of the Heat Credit Value on the Operating Profit of the SO_2 Recovery System

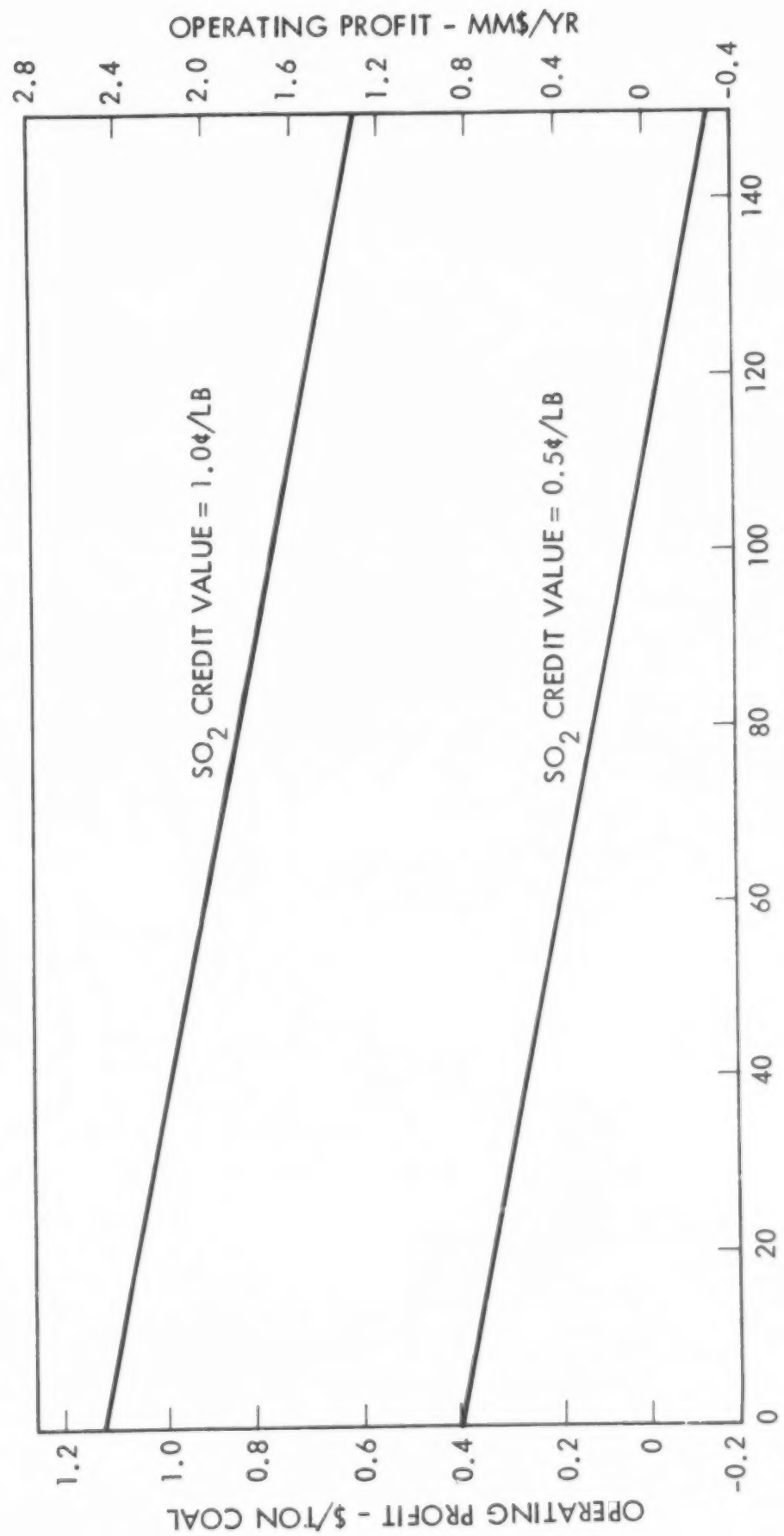


Figure 29. Effect of the Cost of a General Sorbent on the Operating Profit of the SO_2 Recovery System

4.0 APPENDIX - COMPUTER PROGRAM LISTING

```
      DIMENSION X(201,2),Y(201,2),FX(201)
10    ACCEPT 15, AREA,ZFINAL,P,TEMP,FSC,S02PC,YFINAL,QSAT,DEN,E,XKGA,H
15    FORMAT (4E12.6)
      C0 = S02PC * P/(10.73 * (TEMP + 460.))
      G = QSAT/64.
      F = FSC * 14.7 * (TEMP + 460.)/(P * 520. * AREA)
      SFINAL = E*ZFINAL/G
      TYPE 20, SFINAL
20    FORMAT(/E12.6,//,'INPUT - IS,IFLAGS,/)
      ACCEPT 25, IS,IFLAG
25    FORMAT (2I4)
      AH = SFINAL/IS
      AK = 1./60.
      CONY = (C0 * XKGA)/(DEN * G)
      CONX = (XKGA * H)/DEN
      CONST = (XKGA * H * G)/(E * C0)
      TYPE 30, AK,AH,CONY,CONX,CONST
30    FORMAT(//5(F10.4,2X)//)
      IT = 1
      IS=IS+1
      THETA = 0.
      DO 100 N=1,IS
100   X(N,1) = 0.
      Y(1,1) = 1.
      DO 150 N=2,IS
150   Y(N,1) = 0.
200   S=0.
      ID=1
      Y(1,2) = 1.
      X1 = X(1,1)
      DX1 = CONY * Y(1,1) - CONX * X(1,1)
      LX=DX1
202   X(1,2) = X(1,1) + DX * AK
      IF((X(1,2)-X1) - 1.E-2)204,204,203
203   DX2 = CONY * Y(1,2) - CONX * X(1,2)
      DX = 0.5 * (DX1 + DX2)
      X1 = X(1,2)
      GO TO 202
204   IF(X(1,2)-1.)210,205,205
205   X(1,2)=1.
      Y(1,2)=1.
210   IF(IFLAG)225,225,215
215   IF(IT-30)225,220,220
220   TYPE 275, Y(1,2),X(1,2),S
225   DO 260 M=2,IS
      X1 = X(M,1)
      Y1 = Y(M-1,2)
      DX1 = CONY * Y(M,1) - CONX * X(M,1)
      DY1 = -(XKGA/E * Y(M-1,2) - CONST * X(M-1,2))
```

```
    DX=DX1
    DY=DY1
230 X(M,2) = X(M,1) + DX * AK
    Y(M,2) = Y(M-1,2) + DY * AH
    IF((X(M,2) - X1) - 1.E-2)235,235,240
235 IF((Y(M,2) - Y1) - 1.E-2)245,245,240
240 DX2 = CONY * Y(M,2) - CONX * X(M,2)
    DY2 = -(XKGA/E * Y(M,2) - CONST * X(M,2))
    DX = 0.5 * (DX1 + DX2)
    DY = 0.5 * (DY1 + DY2)
    X1 = X(M,2)
    Y1 = Y(M,2)
    GO TO 230
245 IF(X(M,2) - 1.)255,250,250
250 X(M,2) = 1.
    Y(M,2) = Y(M-1,2)
255 S=S+AH
    ID=ID+1
    IF(IFLAG)280,280,260
260 IF(IT-30)280,265,265
265 IF(ID-10)280,280,270
270 Z = S * G/E
    TYPE 275, Y(M,2),X(M,2),Z
275 FORMAT (/3(1PE12.6,3X))
    ID=1
280 CONTINUE
    THETA = THETA + AK
    IF(IT-30)320,300,300
300 T = THETA + E/G * ZFINAL
    TYPE 310, Y(IS,2),X(IS,2),T
310 FORMAT (/1PE12.6,3X,1PE12.6,18X,1PE12.6//)
    IT = 0
320 IF(Y(IS,2) - YFINAL)330,400,400
330 DO 340 J=1,IS
    X(J,1) = X(J,2)
340 Y(J,1) =Y(J,2)
    IT = IT+1
    GO TO 200
400 T = (THETA - AK) + E/G * ZFINAL
    IF(IFLAG)430,430,410
410 ZH=0.
    SH=0.
    DO 420 IA=1,IS,10
    TYPE 275, Y(IA,1),X(IA,1),ZH
    SH = SH + (AH * 10.)
420 ZH = SH * G/E
    TYPE 310, Y(IS,1),X(IS,1),T
430 DO 500 JA=1,IS
500 FX(JA) = X(JA,1) * G * DEN * AREA
    AZ = ZFINAL/IS
    TS02 = 0.
```

```
      FX(IS+1)=0.
      JS=(IS+1)/2
      JS=2*JS
      DO 510 KA=3,JS,2
  510 TSO2 = TSO2 + (FX(KA) + 4.* FX(KA-1) + FX(KA-2)) * AZ/3.
      VOL = AREA * ZFINAL
      PAPER = DEN * VOL
      TYPE 520, VOL,PAPER,T,TSO2
  520 FORMAT(////$VOL ABSORBER - FT3$,5X,1PE12.6,/,$LBS PAPER
     1$,14X,1PE12.6,/,$BATCH TIME - HR$,8X,1PE12.6,/,$SO2 REMOVED
     2 - MOLS$,5X,1PE12.6,//)
 4000 TYPE 5000
 5000 FORMAT(///$INPUT PAPER COST, SO2 VALUE, HEAT COST$/)
      ACCEPT 5010,PAPTON,SO2VAL,HTCST
 5010 FORMAT(3F14.4)
      IDIA=0
      D=(AREA*4./3.1416)**0.5
      D=D*12.
      IF(D-200.)6020,6020,6010
 6010 DA=D
      D=200.
      IDIA=1
 6020 COLCST=((((D*2.515E-06-8.899E-04)*D+0.1182)*D-1.079)*D+82.09)
     1*ZFINAL*2.93*2.0
      IF(IDIA)6030,6040,6030
 6030 COLCST=COLCST*((DA/D)**0.67)
 6040 PAPCST=PAPER*PAPTON/2000./T
      PAPCR=PAPER*7560.*HTCST/1.0E+06/T/100.
      TOTCAP=3.5*COLCST+3.5E+04
      CAPHR=0.2*TOTCAP/7920.
      SO2CR=TSO2*64.066*SO2VAL/100./T
      OPER=25.25
      REGEN=TSO2*64.066*1000.*HTCST/1.0E+06/T/100.
      OPCOST=PAPCST+CAPHR+REGEN+OPER-PAPCR-SO2CR
      TOTYR=OPCOST*7920.
      PAPYR=PAPER*7920./2000./T
      SO2YR=TSO2*64.066*7920./2000./T
      TYPE 6000,TOTCAP,OPCOST,SO2CR,PAPCR,TOTYR,PAPYR,SO2YR
 6000 FORMAT(/////$SUMMARY$//$TOTAL CAPITAL COST = $,3X,1PE14.6,
     1/$OPERATING COST $9H($/HR) = ,1PE14.6,/$SO2 CREDIT $9H($/HR) = ,
     24X,1PE14.6,/$PAPER CREDIT $9H($/HR) = ,2X,1PE14.6,/$TOTAL YEARLY
     3COST = $,4X,1PE14.6,/$PAPER USAGE (TONS/YR) = $,1PE14.6,
     4/$SO2 RECOVERED (T/YR) = $,1X,1PE14.6,/////)
      TYPE 6500
 6500 FORMAT($MORE ? $)
      ACCEPT 6600,IND
 6600 FORMAT(I1)
      IF(IND)6700,6700,4000
 6700 CALL EXIT
      END
```

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